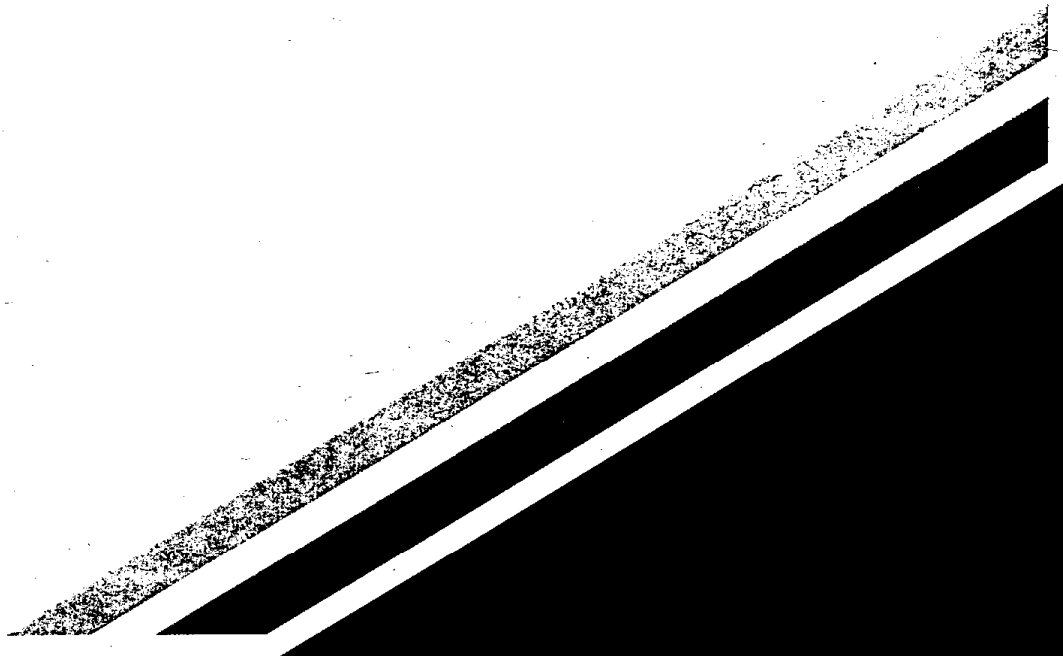




CONTRACT NO. 95-313
FINAL REPORT
AUGUST 1999

Evaluation of Fuel Cell Reformer Emissions



CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



AIR RESOURCES BOARD
Research Division

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EVALUATION OF FUEL CELL REFORMER EMISSIONS

**FINAL REPORT
CONTRACT No. 95-313**

PREPARED FOR:

**CALIFORNIA AIR RESOURCES BOARD
RESEARCH DIVISION
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AUGUST 1999

Evaluation of Fuel Cell Reformer Emissions

Executive Summary

Contractor: ARCADIS Geraghty & Miller
Boeing North America, ETEC

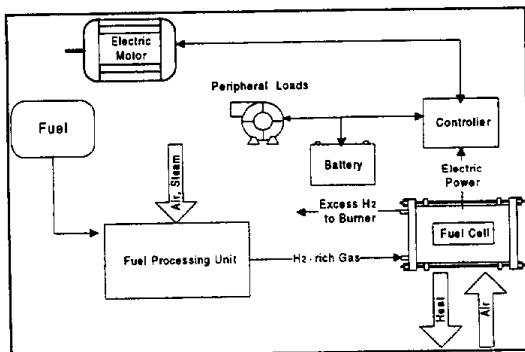
Cosponsors: California ARB, SCAQMD

Background

Zero emission vehicles (ZEVs) are an important part of California's vehicle emission standards. Battery powered electric vehicles represent an initial market entrant, but they have performance limitations that inhibit their wide spread acceptance. The ARB is considering adopting the definition of a ZEV-equivalent vehicle that would include fuel-cell powered vehicles with on-board fuel processors. Fuel cells use hydrogen to produce electricity for electric motors and battery charging. The fuel processor reforms conventional fuels into hydrogen. While the fuel cell produces no emissions, the fuel reformer can produce emissions of CO and NMOG. In this study, the emissions from fuel cell/reformer systems in vehicle applications are compared to emissions from internal combustion vehicles and from the electric power plants needed to charge vehicle batteries.

Technology Description

A schematic of the fuel cell system follows.



Fuels such as gasoline, methanol, natural gas, ethanol, and others can be converted to hydrogen in the fuel processor. Fuel processors operate either on a partial oxidation (POX) or steam reforming principle. Steam reformers can operate at low temperatures with methanol. All other fuels require a reformer that operates at temperatures over 700°C. Because steam reformers require heat transfer between a burner and the reformed fuel, high temperature steam reformers are not practical for passenger cars.

A POX system with a proton exchange membrane fuel cell (PEMFC) fuel cell is well suited for a variety of fuels and can be packaged for passenger cars. A PEMFC has the added advantage of operating at low temperatures and is not adversely affected by changes in load and start/stop operation. A disadvantage of the PEMFC is that its performance degrades in the presence of the CO, which is produced in reformers. A fuel processor unit would consist of a POX reactor integrated with catalysts that remove CO. The gas mixture contains about 33 percent hydrogen and is fed to the PEMFC. Most of the hydrogen is converted to electricity, but about 20 percent exits the fuel cell where it is combusted in a burner with the energy used to power an air compressor.

Scope

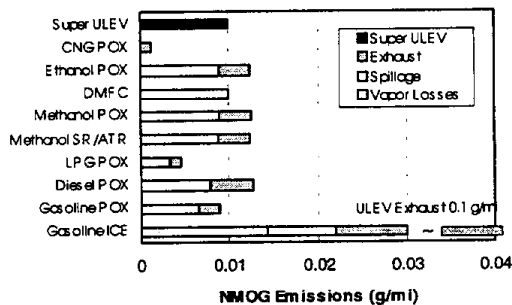
This project included:

- Evaluation of fuel cell and reformer technologies in current development
- Development of realistic light and heavy-duty vehicle cases for performance and emission modeling
- Collection of emission data
- Comparison of emission estimates to existing vehicles and future standards

Findings — Light-duty vehicles

The results of this assessment indicated that multi-fuel partial oxidation reformers with PEMFCs are practical candidates for passenger vehicles. Solid oxide fuel cells (SOFCs) and direct methanol fuel cells (DMFCs) are not near-term options. These Technologies require further development to scale up to a size that is suitable for vehicle applications.

Emissions from PEMFC vehicles can be lower than ARBs proposed SULEV standard, assuming that vapor losses are eliminated. NO_x emissions are inherently low, but control of NMOG emissions is required for some fuel processor systems. Refueling spillage and exhaust NMOG put some vehicles at or above the standard as shown below.



The emissions from burning the fuel cell anode gas of a PEMFC are almost below detection levels. The primary source of NMOG and CO emissions is the warm up burner during start-up. Natural gas POX/PEMFC vehicles can meet the standard with little or no emission control since natural gas is primarily composed of methane and contains few higher hydrocarbons. NMOG emissions will likely need to be controlled from POX/PEM systems operating on other fuels and methanol steam reformers.

Low temperature methanol steam reformer PEMFC systems are more efficient than POX/PEMFC systems, but methanol fueling infrastructure is not widespread. A high purity methanol will likely be required for low-temperature steam reformers.

Findings — Heavy-duty vehicles

Case studies for heavy-duty vehicles included a PEMFC system with low temperature methanol steam reformers, phosphoric acid fuel cell with a high temperature reformer operating on methanol and natural gas, PEMFC with diesel POX, and an SOFC with a POX fuel processor.

NO_x , CO, and NMOG emissions from fuel cell powered buses are demonstrated to be far below those from diesel buses. As indicated in the figure below, NO_x levels are as low as one-hundredth of diesel levels. NMOG levels are one tenth of diesel levels with modest exhaust gas clean-up.

Fuel cell operation results in a 20 to 30 percent improvement in fuel economy which translates directly to a 20 to 30 percent reduction in CO_2 emissions.

A final report for the project is available.

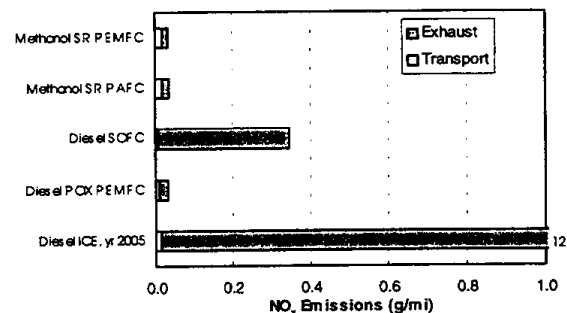


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NOMENCLATURE

Symbols and Abbreviations

A	Amperes
ADL	Arthur D. Little
ART	Arterial driving cycle
atm	absolute pressure in atmospheres
ATR	autothermal reactor
Btu	British Thermal Units, 1 Btu = 1055 J
C	Centigrade, $^{\circ}\text{C} = \text{K} - 273$
CBD	Central Business District driving cycle
CNG	compressed natural gas
DMFC	direct methanol fuel cell
DOD	United States Department of Defense
DOE	United States Department of Energy
DOT	United States Department of Transportation
EPA	United States Environmental Protection Agency
ERC	Energy Research Corporation
η	eta, efficiency
F	Fahrenheit $^{\circ}\text{F} = ^{\circ}\text{C} \times 9/5 + 32$
FC	fuel cell
FTA	Federal Transit Administration
FUDS	Federal Urban Driving Schedule
g	gram
gal	gallon, 1 gal = 3.785 L
h	hour
HBT	Hydrogen Burner Technology
HHV	higher heating value
HTS	high temperature shift reactor
IFC	International Fuel Cells
J	Joule
K	Kelvins
km	kilometer
kW _e	kiloWatts of electric energy
kWh	kiloWatt hour 1 kWh = 3412 Btu
λ	lambda, stoichiometric ratio
L	liter
LHV	lower heating value
LPG	liquefied petroleum gas
LTS	low temperature shift reactor
m	meter
MCFC	molten carbonate fuel cell
mi	mile, 1 mile = 1.61 km
mpg	miles per gallon

NOMENCLATURE (CONTINUED)

mph	miles per hour
MW	molecular weight
NL/h	standard or normal liters per hour
PAFC	phosphoric acid fuel cell
PEMFC	proton exchange membrane fuel cell
POX	partial oxidation
ppm	parts per million
PROX	preferential oxidizer
PSA	pressure swing adsorption
RFG	reformulated gasoline
RVP	Reid vapor pressure (vapor pressure of liquids at 100°F)
s, or sec	second
SCAQMD	South Coast Air Quality Management District
SOC	battery state of charge
SOFC	solid oxide fuel cell
SR	steam reformer
SV	Space velocity
TBB	Test Bed Bus
UOB TM	Underoxidized burner from HBT
V	Volts
W	Watt, 1W = 1 J/s

Metric Size Designations

G	giga, 1,000,000,000
M	mega, 1,000,000
k	kilo, 1000
m	milli, 10 ⁻³

Compounds, Chemicals, and Pollutants

C(s)	solid carbon
CH ₄	methane
CO	carbon monoxide
CO ₂	carbon dioxide
H ₂	hydrogen
HCHO	formaldehyde
K ₂ CO ₃	potassium carbonate
La _{1-x} Sr _x MnO ₃	strontium doped lanthanum manganite
Li ₂ CO ₃	lithium carbonate

NOMENCLATURE (CONCLUDED)

Ni	nickel
NiO	nickel oxide
NMOG	non-methane hydrocarbons
NO _x	oxides of nitrogen
Pt	platinum
Ru	ruthenium
THC	total hydrocarbons
Y ₂ O ₃ • ZrO ₂	yttria stabilized zirconia
ZrO ₂	zirconium oxide

1. INTRODUCTION

Fuel cells directly convert the chemical energy from the oxidation of hydrogen into electrical energy. With this process, energy conversion efficiencies on the order of 80 percent are theoretically possible. In comparison, the theoretical energy conversion efficiency for a fuel burning piston engine-generator is generally limited to less than 50 percent while somewhat greater efficiencies are possible with combined cycle systems. The use of fuel cells offers the added potential of a mobile power source with low emission characteristics.

Over the past 30 years, certain types of fuel cells were developed and used extensively for the U.S. space program. Unfortunately, fuel cells suitable for space applications are poor candidates for vehicle use, because the need to generate and supply hydrogen gas produces fuel handling, storage, and safety problems.

1.1 PROGRESS IN FUEL CELLS

Worldwide, numerous programs are underway to adapt fuel cell technology to the constraints of light duty and heavy-duty vehicle operation. In the U.S., the Department of Energy's Partnership for a New Generation Vehicle (PNGV) recently announced breakthroughs towards its goal "to develop technology that leads to a passenger automobile with 80 miles per gallon fuel economy." The DOE asserts that "the new technology converts the gasoline or alternative fuel into the hydrogen needed for the fuel cell to produce electricity." The DOE also states that "the technology is clean and efficient, with emission levels much lower than California's Ultra-Low-Emission Vehicles Standard. . ."

Considerable interest also exists within the automobile industry. For example, Daimler Benz has boldly announced that they will have 100,000 fuel cell vehicles on the road by 2005. They have formed a joint venture with Ballard Power Systems and Ford to make this happen. Daimler Benz has also demonstrated a zero-emission, stored-hydrogen, fuel cell vehicle, called NECAR II, and more recently has shown their new "A" class urban vehicle (NECAR 3) equipped with a methanol reformer fuel cell system to help address range and refueling infrastructure issues.

1.2 EMISSION STANDARDS

The South Coast Air Quality Management District (SCAQMD) has implemented a clean fuels program and also has specific inventory reduction goals. Fuel cell powered vehicles can play a role in providing further emission reductions particularly in crowded urban areas where particulate emissions are a more important issue and regions where attaining ozone standards requires controlling NO_x and hydrocarbon emissions.

Fuel cell vehicles can also play an important role in helping automobile manufacturers comply with the Low Emission Vehicles (LEV) rule that was adopted by the California Air Resources Board (ARB) in 1990. The rule is designed to further the development of low emission technologies. The LEV rule calls for fleet average emission limits and for a percentage of new vehicles in 2003 to be zero emission vehicles (ZEVs). A ZEV is defined as a vehicle that produces no emissions during any operating condition throughout its life. Battery-powered electric vehicles (EVs) and dedicated hydrogen fuel cell vehicles are considered to be true ZEVs. Fuel-cell-powered vehicles with fuel reformers may qualify as ZEV equivalents.

Table 1-1 shows the LEV exhaust standards applicable to all Transitional Low-Emission Vehicles (TLEVs); Low-Emission Vehicles (LEVs); Ultra-Low-Emission Vehicles (ULEVs); and Super-Ultra-Low-Emission Vehicles (SULEVs).

Table 1-1. Existing and proposed LEV exhaust emission standards (g/mi)

Vehicle Category	Vehicle Durability (miles)	NMOG	Carbon Monoxide	Oxides of Nitrogen	Particulate Matter ^a	Formaldehyde
TLEV	50,000	0.125	3.4	0.4	NA ^b	0.015
	120,000	0.156	4.2	0.6	0.04	0.018
LEV	50,000	0.075	3.4	0.05	NA	0.015
	120,000	0.090	4.2	0.07	0.01	0.018
ULEV	50,000	0.040	1.7	0.05	NA	0.008
	120,000	0.055	2.1	0.07	0.01	0.011
SULEV	120,000	0.010	1.0	0.02	0.01	0.004

^aDiesel vehicles only.

^bNA = Not applicable.

The SULEV category would have two separate useful life mileages: 120,000 miles, and an optional 150,000-mile useful life. The 150,000-mile certification would be required for SULEV-certified vehicles to qualify for partial ZEV credits if they met certain criteria.

The addition of the SULEV standard will impact the implementation rates for the reduction of the fleet average NMOG requirements as shown in Table 1-2. Only the fleet average would be a regulatory requirement; manufacturers could choose their own implementation schedule as long as the fleet average requirement is met each year.

Table 1-2. Example implementation percentages for TLEVs, LEVs, ULEVs, SULEVs, and ZEVs used to calculate fleet-average g/mi standards for passenger cars and light-duty trucks

Model Year	TLEV	LEV	ULEV	SULEV	ZEV	Fleet Average NMOG Requirement
2004	2	48	35	5	10	0.053
2005	2	40	38	10	10	0.049
2006	2	35	41	12	10	0.046
2007	1	30	44	15	10	0.043
2008	1	25	44	20	10	0.040
2009	1	20	49	20	10	0.038
2010	1	15	49	25	10	0.035

1.3 PARTIAL ZEV CREDITS

ARB continues to believe that ZEV technologies, such as battery electric vehicles and hydrogen fuel cell vehicles with zero emissions of regulated pollutants, should be strongly encouraged because, unlike other technologies, they do not exhibit emission increases with age. New vehicles must have more durable emission controls and on-board diagnostic systems for effectively alerting owners to problems, and they must meet the Smog Check requirements for emission system maintenance as vehicles age. Despite these monitoring and maintenance requirements, vehicle degradation continues to present problems. Smog Check cost issues may allow continued operation of high emitters; owners may not respond to “check engine” lights promptly; a significant number of cars are not registered; and other problems continue to degrade clean air. ZEVs do not have these kinds of problems. ARB staff, therefore, believes that it is appropriate to create incentives for the cleanest technologies, which provide near-zero emissions, by providing them with partial ZEV credits.

The revised ZEV program allows for additional flexibility to broaden the scope of vehicles that could qualify for meeting some portion of the ZEV requirement. Manufacturers would decide which mix of vehicles to use to meet the 10 percent ZEV requirement, with the exception that large-volume manufacturers would have to meet at least 40 percent of the requirement using true ZEVs. The applicable ZEV allowance for each vehicle type would be determined based on a set of criteria designed to identify and reward ZEV-like characteristics in a variety of advanced-technology vehicles. In order for a vehicle to receive any ZEV allowance, the vehicle would need to satisfy the requirements for receiving the “baseline ZEV allowance.” To receive this allowance, the vehicle would need to meet SULEV standards, satisfy second-generation on-board diagnostics requirements, and zero fuel evaporative emission requirements. A vehicle meeting this requirement would receive a 0.2 ZEV allowance. An additional allowance up to 0.6 is provided for vehicles realizing zero-emissions potential with an extended range. This allowance could apply to hybrid-electric vehicles with battery-only driving capability, or to fuel-cell-

powered vehicles with nil emissions. Vehicles that use fuels with very low fuel-cycle emissions can receive a further ZEV allowance of up to 0.2. The fuel-cycle emissions associated with a particular fuel are the total emissions associated with the production, marketing, and distribution as grams per unit of fuel. The marginal NMOG emissions associated with the fuel use by the vehicle must be lower than or equal to 0.010 grams per mile (g/mi). For the purpose of providing this allowance, fuel-cycle NO_x emissions are not considered in the determination because marginal NO_x emissions for virtually all fuels are uniformly low.

1.4 CALIFORNIA'S ENHANCED EVAPORATIVE AND ONBOARD REFUELING VAPOR RECOVERY EMISSION REGULATIONS ("ZERO-EVAP")

ARB staff is proposing amendments to the enhanced evaporative and refueling standards and test procedures that will establish zero evaporative emission standards and test procedures within the limits of current measurement technology. These regulations are referred to as the "zero-evap" regulations.

The proposed evaporative and refueling regulations would be applicable to gasoline-fueled, liquefied petroleum gas-fueled, alcohol-fueled, and hybrid electric vehicles. Zero emission vehicles with fuel-fired heaters would also be included. ARB staff proposes that vehicles subject to the evaporative emission regulations be required to emit zero evaporative emissions during testing.

1.5 STUDY APPROACH

The purpose of the study reported herein is to assist ARB staff in its evaluation of potential ZEV equivalent factors by assessing the lifetime emissions associated with the use of fuel cells for light and heavy-duty vehicle systems. Emissions from these systems occur due to the conversion of conventional and alternative fuels to hydrogen in an on-board device (reformer) as well as the co-lateral activities associated with the production, transport, and distribution of the fuels. This study includes an analysis of gasoline, diesel, methanol, ethanol, natural gas, liquefied petroleum gas (LPG), and diesel as reformer fuels.

The assessment is accomplished through an evaluation of performance characteristics for current and projected fuel cells and reformer systems (Sections 2 and 3), development of case studies for anticipated vehicle configurations (Section 4), collection of applicable emissions data (Section 5), and evaluation of emission characteristics for the selected case studies (Section 6). An outline of the assessment process is given in Table 1-3. Figure 1-1 is the assessment flow diagram.

Section 2 describes the principles of fuel cell operation and identifies the operating characteristics and design features of current and developmental fuel cell devices. The proton exchange membrane (PEM) fuel cell (PEMFC) has advantages that make it an attractive technology for vehicle applications. It operates at relatively low temperature and is not adversely affected by changes in load or by start/stop operation. The direct methanol fuel cell (DMFC) solves system problems, but further development is required.

Table 1-3. Fuel cell/reformer emission assessment

Parameter	Objective	Scope
Fuel Cell Performance	Assess feasible fuel cells for vehicle applications. Determine voltage - current characteristics of fuel cell stacks to determine load dependent efficiency and fuel processor requirements	Review of fuel cell types Evaluation of PEMFC, DMFC, PAFC, SOFC in vehicles
Fuels	Evaluate reformer options and emissions for various fuels.	Reformulated gasoline (RFG), diesel, LPG, CNG, ethanol, methanol
Fuel Processor Performance	Assess feasibility of fuel processors for vehicle applications Determine fuel processor characteristics, exit gas compositions, gas clean-up requirements, and fuel cell feed gas composition.	Partial oxidation (POX) Steam Reforming (SR) Autothermal reforming (ATR) In-situ direct methanol fuel cell (DMFC)
Fuel Cell/ Fuel Processor Systems	Determine gas flows and composition in fuel cell system Determine inputs to burners Evaluate effects of transient operation.	POX/PROX/PEMFC, multi-fuel Methanol SR/PEMFC Methanol SR/PAFC DMFC POX/SOFC diesel
Vehicle configuration	Determine vehicle weight and system energy consumption.	LDV with full power fuel cell Hybrid LDV Transit bus with full power fuel cell Hybrid transit bus
Emission Data	Assess emissions from fuel cell system burners. Generate input for system energy model. Determine cold start emissions.	PAFC bus emissions, POX composition data, POX flare data, Anode gas burner data, Conventional fuel burner data
System Energy Model	Determine fuel cell power requirement over vehicle driving cycle Combine vehicle requirements and fuel processor performance map to determine burner emissions.	FUDS, ECE, HFET driving cycles for LDVs. CBD and Schedule D driving cycles for buses.
Emission Analysis	Assess the emissions from LDV and HDVs Compare to standard vehicle emissions Evaluate ability of fuel cell powered vehicles to meet emission levels similar to ZEVs.	NO _x , NMOG, CO, CO ₂ from vehicle exhaust Local fuel cycle NMOG and NO _x emissions Global CO ₂ emissions.

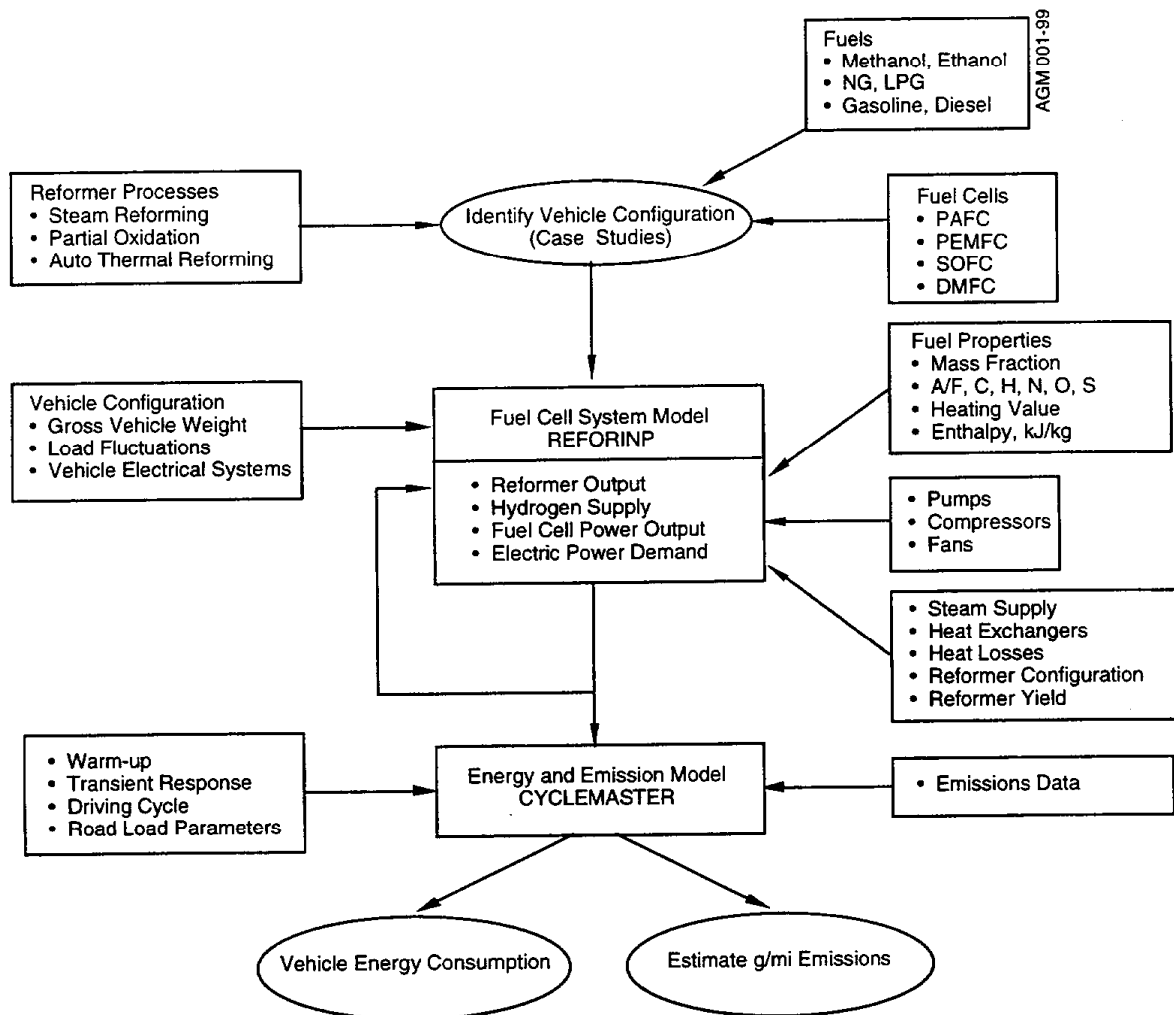


Figure 1-1. Fuel cell/reformer emission assessment process

Section 3 provides extensive information on the fundamental operating parameters, design features, and performance tradeoffs among candidate reformers for on-board conversion of fuels to hydrogen. Steam Reformer (SR) and Partial Oxidation (POX) reforming technologies are generally well developed for the petrochemical industry. Equipment development is in progress to revise and adapt reformers to the constraints of vehicle operation and the fuel cell interface. Methanol SRs have an advantage in vehicle applications, because they operate at lower temperature. POX systems operate at higher temperatures, but are effective in converting a variety of fuels without the need for additional burners to preheat the fuel, air, and steam.

In Section 4, the vehicle design implications of using reformer/fuel cell systems in light and heavy-duty vehicle applications are described through the development of case studies. Vehicle weight implications and energy consumption scenarios are presented for referenced vehicle duty cycles. In addition to providing size factors for various applications, the results in Section 4

identify fuel usage and fuel economy factors that will enable comparison of emission estimates to emissions standards and emissions from conventional vehicles.

Section 5 summarizes the emission data that were generated for this project and that were available in literature sources. Data were obtained from a methanol-fueled, fuel cell bus systems, from a stationary reformer system, and from laboratory and literature emission data sources. The emission data are compared on the basis of grams of emissions per unit energy input to the reformer burner. Reformer burners emit substantially less oxides of nitrogen, and somewhat less carbon monoxide and total hydrocarbons than conventional burners, because the reforming occurs at low temperatures.

The results of the emission assessment for the various vehicle cases are given in Section 6. Figure 1-1 shows the steps in determining emissions. Vehicle case studies from Section 4 are used as inputs to a REFORINP fuel cell system model which determines the energy consumption over a range of fuel cell loads. The mass of vehicles are combined with the fuel cell efficiency, reformer efficiency, fuel cell performance curve, and vehicle driving cycle in the CYCLEMASTER energy and emissions model. The vehicle fuel consumption and gram per mile emissions are then determined. Figure 1-2 illustrates some of the key inputs to this process. The vehicle configuration determines the vehicle weight. The amount of hydrogen produced per unit of fuel is affected by the fuel processor performance curve which affects reformer efficiency. The fuel cell performance curve determines the efficiency over different load conditions.

The study demonstrated conclusively that emissions from the fuel cell/reformer systems analyzed in this report are substantially below the levels of conventional light duty and heavy-duty vehicles. In comparison to the power plant emissions associated with the ZEV, the conclusion is that additional research into reformer design and operation is needed to firmly establish specific ZEV-equivalent factors for fuel cell systems. Section 7 expands on these conclusions.

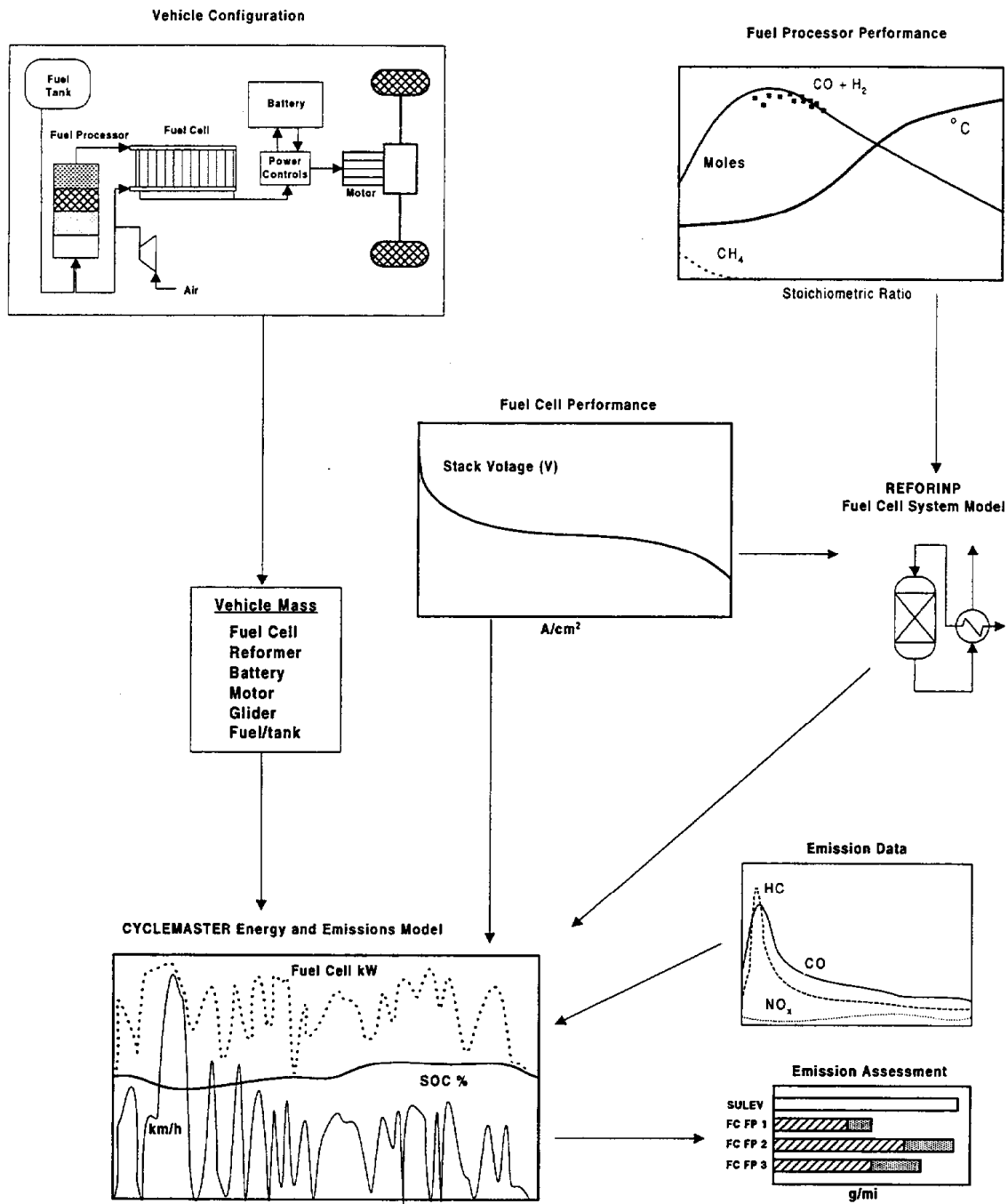


Figure 1-2. Emission assessment inputs

2. FUEL CELL OPTIONS AND PERFORMANCE CHARACTERISTICS

The operating conditions and reactant requirements for fuel cells affect their suitability for vehicle applications and also affect the reformer and fuel processing requirements. This section describes different types of fuel cells, their use in vehicle applications, and typical operating characteristics. Fuel cell performance requirements determine the size and weight of the fuel cell and fuel processor and, consequently, affects vehicle weight, fuel consumption, start up requirements, and emissions. The fuel cell performance parameters are needed for the integrated fuel cell/fuel processor model that leads to estimates for fuel consumption and emissions.

2.1 PRINCIPLES OF FUEL CELL OPERATION

Fuel cells generate electric power through an electrochemical reaction in the same manner as batteries. Unlike a battery in which the chemical components are eventually depleted, a fuel cell produces power as long as a stream of reactants is available. Fuel cells have the potential to generate electrical energy or work more efficiently than heat engines or mechanical processes. In addition, because fuel cells and fuel processors operate at temperatures lower than heat engines, emissions of NO_x are virtually eliminated.

The high efficiency of a fuel cell arises from its ability to convert much of the energy released by the reactants directly into an electrical energy. The energy associated with the flow of electrons is largely available for conversion to shaft work. In contrast, when fuel is burned to heat and expand a gas in a heat engine, the motion of the gas molecules is random, and therefore less available to accomplish useful work (Thomas 1989).

The electrical work from a fuel cell also depends upon the conditions for producing electrical current. The voltage (which is proportional to the efficiency) is limited by the activation energy of the fuel cell reactants, resistive heating in the fuel cell media (ohmic losses), and mass transfer across the fuel cell media. These kinetic aspects of fuel cells result in losses referred to as overvoltage or polarization.

The basic elements of a typical fuel cell are shown in Figure 2-1. The example is a phosphoric acid fuel cell (PAFC) that includes an anode, cathode, electrolyte, and electric load. Many different reactants can be used to generate power in a fuel cell. Hydrogen/air systems are most commonly considered for vehicle applications. Other types of fuel cells are discussed later. In a hydrogen system, the electrodes are commonly immersed in an electrolyte consisting of a strong acid or base. Fuel (hydrogen gas) is admitted at the anode while oxidant (oxygen or air) enters at the cathode. The electrodes are typically porous and coated with catalysts. Increasing the porosity of the electrode increases its surface area, and hence, also increases the current that it

can support at a given temperature. Rates of fuel cell reactions increase strongly with temperature. Oxygen has a much greater affinity for electrons (electronegativity) than hydrogen. This electronegativity difference gives rise to a potential difference between the electrodes of 1.25 V at 1 atm and 85°C. The voltage efficiency of the fuel cell is thus the actual voltage between the cathode and anode divided by 1.25V.

$$\eta_v = \Delta V / 1.25 \text{ V}$$

This potential difference causes hydrogen to ionize to H^+ at the anode:



Electrons are conducted across the load to the cathode. Hydrogen ions (protons) formed at the anode diffuse into the electrolyte solution separating the anode and cathode. At the cathode, oxygen, hydrogen ions, and electrons combine to form water:

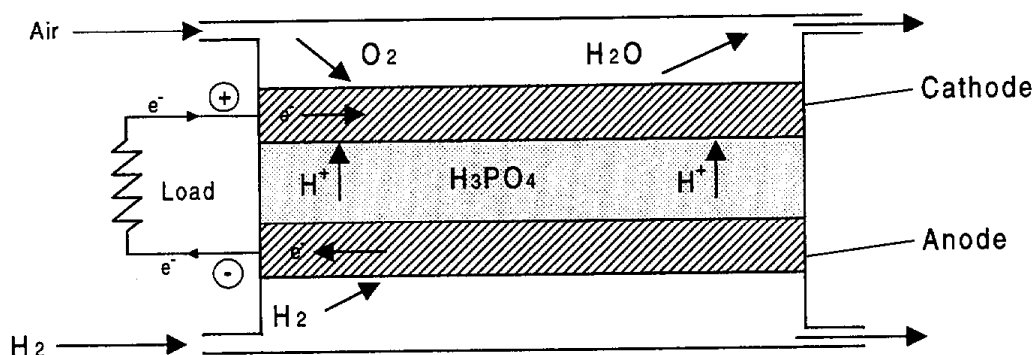
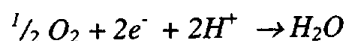


Figure 2-1. Operation of a phosphoric acid fuel cell

The complete circuit in a fuel cell consists of two phases:

- Flow of electrons down the potential difference from the anode through a conductor and across the load to the cathode
- Flow of hydrogen ions from anode down the concentration gradient in the electrolyte to the cathode.

The overall chemical reaction of the fuel cell combines hydrogen with oxygen to produce water. Because the process can take place at low temperatures, the fuel cell may be viewed as a device that achieves cold oxidation of hydrogen.

The ideal efficiency of hydrogen-oxygen fuel cells can be over 80 percent at low current levels. The actual efficiency of practical cells is less. The reduction of efficiency arises from voltage losses that occur when the cell moves from an open circuit condition and begins to conduct a current. These losses include:

- A potential difference (polarization) between the electrolyte and the cathode, that arises in order to drive the flow of oxygen ions out of the cathode
- Inability of ion current to increase in direct proportion to decreases in load resistance
- Internal cell resistance resulting in ohmic heating.

The extent of these losses can be seen in the polarization curves for different types of fuel cells in the following sections. Because of these losses, as well as auxiliary loads such as water pumps, air fans or other coolant pumps, actual efficiencies of working fuel cells are in the range of 40 to 60 percent.

2.2 FUEL CELL TECHNOLOGIES

Fuel cells vary according to their reactants, operating temperature, type of electrolyte, and other parameters. Table 2-1 shows fuel cells that are practical candidates for power production.

Alkaline fuel cells (AFC) have been used extensively in the United States' space programs, but have properties which make them poor candidates for automotive use. Both phosphoric acid cells (PAFCs) and proton exchange membrane fuel cells (PEMFCs) are being investigated in North American fuel cell bus development programs while the PEMFCs are the leading candidates for passenger car use. Direct methanol fuel cells (DMFCs) are a variation on the PEMFC which uses liquid methanol as a reactant rather than hydrogen but they are still in the early development stage.

Molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) operate at elevated temperatures. Fuel processing and hydrogen production may be accomplished within the fuel cell because it operates at such high temperatures. High temperature fuel cells are generally not a first choice for light-duty vehicle applications because they need to ramp up to temperature prior to operation. In addition, thermal cycling that would be encountered with turning the fuel cell system on and off adversely affects durability. MCFCs are too bulky for vehicle applications; however, SOFCs may be suitable for packaging in the size range required for vehicle operation. The important characteristics of each type of fuel cell and their applicability for vehicle operation are reviewed in the following sections.

Table 2-1. Typical fuel cell characteristics and operating conditions (BÆgild Hansen, Rostrup-Nielsen)

Parameter	Low-Temperature Fuel Cells				High-Temperature Fuel Cells	
Cell Type ^a	AFC	PAFC	PEMFC	DMFC	MCFC	SOFC
Temperature (°C)	60 to 120	150 to 250	80 to 100	80 to 120	650	900 to 1100
Electrolyte	KOH	H ₃ PO ₄	Polymer	Polymer	(K, Li)CO ₃	Y ₂ O ₃ , ZrO ₂
Anode Fuel	High purity H ₂	H ₂	H ₂	CH ₃ OH, H ₂ O	CH ₄ to H ₂ , CO	CH ₄ to H ₂ , CO
Cathode Feed	High purity O ₂	Air	Air	Air	Air + CO ₂	Air
Anode Catalyst	Pt	Pt	Pt	Pt	Ni	Ni/ Zr ₂ O ₃
Cathode Catalyst	Pt	Pt	Pt	Pt	NiO	La-Sr-MnO ₃
Cell efficiency ^b	50 to 60	55	50 to 60	40 to 50	60 to 65	55 to 65

^a AFC = Alkaline Fuel Cell, PAFC = Phosphoric Acid Fuel Cell, PEMFC = Proton Exchange Membrane Fuel Cell, DMFC = Direct Methanol Fuel Cell, MCFC = Molten Carbonate Fuel Cell, SOFC = Solid Oxide Fuel Cell.

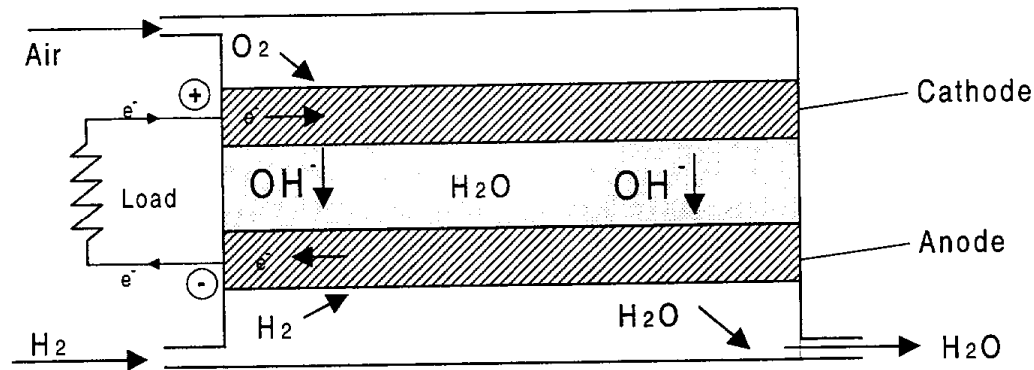
^b Cell voltage efficiency (Kordesch, 1996)

2.3 ALKALINE FUEL CELLS (AFC)

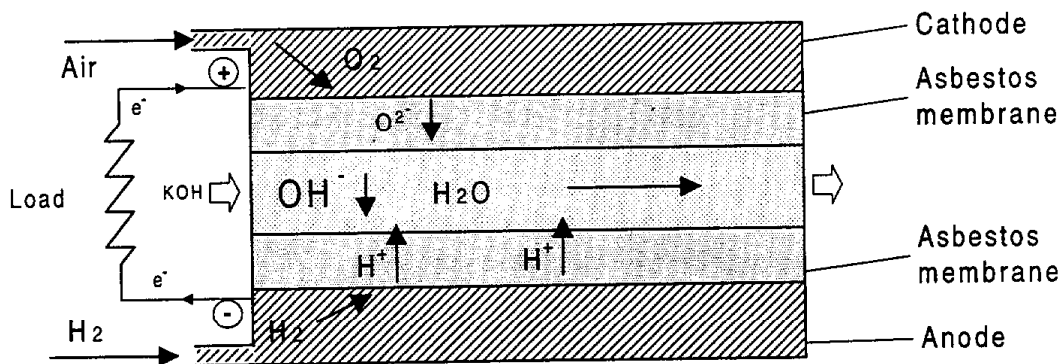
Intensive development for the Apollo and Space Shuttle programs has resulted in extensive development of AFC technology. The electrolyte for AFCs is a strong base, such as potassium hydroxide. The charge carrier in the electrolyte solution is the hydroxide radical (OH⁻), rather than the hydrogen ion (H⁺) as shown in Figure 2-2. Alkaline electrolytes have a low activation energy for the cell reactions, enabling them to start up from ambient temperatures without the need for preheat. Heat generated within the cell can then be used to elevate its temperature, thereby increasing its power density. Power density can also be increased by increasing the fuel and oxidant pressures. The Apollo program used high temperature, high pressure cells developed by United Technology Corporation (UTC). UTC then developed an improved alkaline cell for the Space Shuttle, which operates at low temperature (about 85°C) and a pressure of 4 atm.

AFC's ability to operate at low temperatures enables them to start up rapidly. This feature, along with high power density, makes this technology attractive for transportation applications. In an AFC, carbon dioxide precipitates as carbonate which deactivates the cell. Atmospheric air contains about 350 ppm of CO₂. The CO₂ reacts with the potassium hydroxide electrolyte to produce a solid, potassium carbonate. The response to CO₂ makes the alkaline cell unsuitable for use with reformed hydrocarbon fuels and therefore, pure hydrogen must be used. If atmospheric air is used as the oxidant, essentially all of the CO₂ present in the air stream must be removed before it is fed to the cell.

Since AFCs are very limited with their requirements for fuels and oxidants they are not suitable for vehicle applications. CO₂ removal from air would require bulky clean up systems. Extensive clean-up of the hydrogen fuel would also be required.



Alkaline fuel cell with static electrolyte



Alkaline fuel cell with recirculating electrolyte

Figure 2-2. Operation of an alkaline fuel cell

2.4 PHOSPHORIC ACID FUEL CELLS (PAFC)

Unlike alkaline electrolytes, acidic electrolytes do not react with carbon dioxide to form carbonate. This property makes them suitable for use with gases containing carbon dioxide, such as the products of a reformer (reformat) that is fed with natural gas or methanol and air. This is the major advantage of acid-electrolyte fuel cells over alkaline cells.

In addition to CO_2 , reformat gas normally contains some residual CO . At low temperatures, CO strongly adsorbs onto the platinum catalysts on the cell electrodes, thereby deactivating them. However, CO adsorption decreases as the fuel cell temperature increases, enabling it to be controlled by increasing operating temperatures. Therefore, PAFCs operate in the region of 130 to 200°C to minimize the effect of CO on efficiency. Among the strong acids, phosphoric acid is uniquely stable at these high temperatures, and also has high ionic conductivity. These were the main reasons that phosphoric acid was chosen as the electrolyte for an acid fuel cell. A drawback of this choice is that phosphoric acid cells are inoperable at room temperature, and must be preheated. Ordinarily, a hydrocarbon-fueled auxiliary burner is used for this purpose. The

operating temperature range of PAFCs is necessary to maintain ionic conductivity of the electrolyte and also reduce CO adsorption.

Fuel cells can be the basis of very efficient co-generation systems for utility customers who require both electricity and heat. Phosphoric acid fuel cells (PAFCs) were developed in response to the desire of the natural gas utilities to expand sales of natural gas by generating electricity in "on-site" power plants located at shopping malls, industrial complexes, etc., where both the electricity and the rejected heat could be used. The waste heat from PAFCs is at a relatively low temperature and would ideally be suited for integration with hydronic heating systems. PAFCs can also generate low quality steam for absorption cooling.

The initial development of the PAFC technology took place at the Power Systems Division of United Technologies (formerly Pratt and Whitney) presently International Fuel Cells, Inc. It led to fuel cell stacks of about one square foot of area and 100-200 individual cells operating at a current density of 100-200 mA/cm². The stacks had a nominal operating temperature of 190°C and were cooled with a steam/water mixture, which was also used in some cases for heating purposes. The fuel and air streams were at ambient pressure. With strong acid electrolytes, electrode dissolution over time is a potential problem. Graphite electrodes were found to be very resistant to attack. Platinum makes an effective catalyst since it resists corrosion and results in a high cell voltage output. Because of platinum's high cost, research has concentrated on minimizing platinum loadings. 1 mg/cm² is now routine, corresponding to 5g/kW. At the current market price of platinum (\$10 to \$12/g), this is equivalent to \$50/kW.

The second generation of PAFC cells was developed by International Fuel Cells under sponsorship of the Electric Power Research Institute (EPRI) and the United States Department of Energy (DOE). These cells operate at elevated pressure, so as to increase their voltage and current density. Both the fuel and oxidant streams are compressed to about 7 atm. Pilot plants of 4.5 MW_e and, later, of 11 MW_e, operating on natural gas, have been designed and built (Yolota). The PAFC technology developed by IFC are now available for commercial sale. IFC produces a 200 kW PAFC which it markets through its ONSI subsidiary as the PC25. Over 160 units have been installed and some units have operated over 40,000 hours. Establishing commercial viability now hinges on achieving substantial reductions in manufacturing costs. IFC has also developed a 100 kW transportation PAFC. PAFC fuel cells have long been projected to become cost competitive when production rises to 200-300 MW per year (Teagan). Fuel cells are currently cost effective for stationary power generation in areas such as New York City where the combination of high electricity prices and stringent permit requirements provide an advantage for the fuel cell (Barrigh).

Data from IFC indicates that fuel cells can be very reliable and require low maintenance. The electric power from fuel cell generation systems is considered "clean" and does not contain fluctuations in frequency or other power distortions that would affect sensitive equipment such as computers. IFC is also developing a 100 kW PAFC for bus applications.

Other PAFC manufacturers include Fuji Electric, Mitsubishi Electric, and Toshiba. A 57 kW Fuji PAFC was installed on 3 transit buses in a program with DOE, DOT, SCAQMD, and

Georgetown University. The fuel cell operated on reformat from a methanol steam reformer. This system is discussed in great detail in Section 4.

Figure 2-3 shows the cell voltage performance of an IFC PAFC (IFC 1992). This chart shows the voltage for each cell and polarization losses as the voltage drops with increasing current draw. As fuel cell performance improves with development, the improvements in efficiency are reflected by an increasingly linear polarization curve. The project cell voltage in Figure 2-3 is based on the targets. Figure 2-4 shows the power density which is the product of the cell voltage and current density. As indicated, a PAFC produces about 0.23 W/cm^2 , which is within the design targets of PAFC developers (Kordesch). PAFCs operate at relatively low current densities compared to PEMFCs and SOFCs which indicates that a PAFC will likely be more bulky than other types of fuel cells.

PAFC performance is reduced when the fuel cell is fed with reformer effluent. The reduction in performance arises from dilution as well as with CO_2 and CO . The performance of PAFC operating on reformat is less than that of a PAFC operating on pure hydrogen. Data from Energy Research Corporation (1990) shown in Table 2-2 indicate the reduction in voltage output of a 1.8 kW PAFC with reformer products.

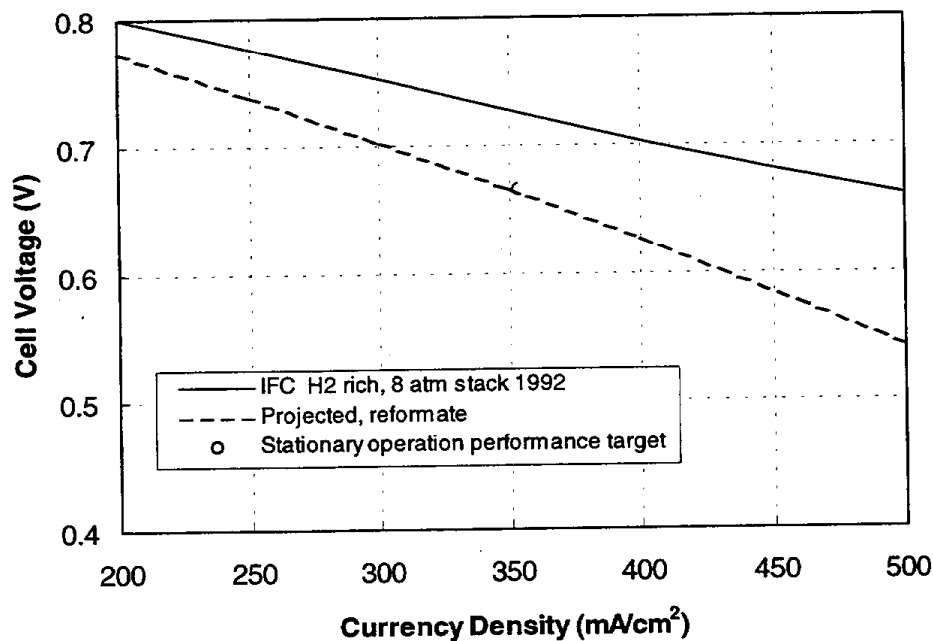


Figure 2-3. PAFC fuel cell stack performance, reformat operation

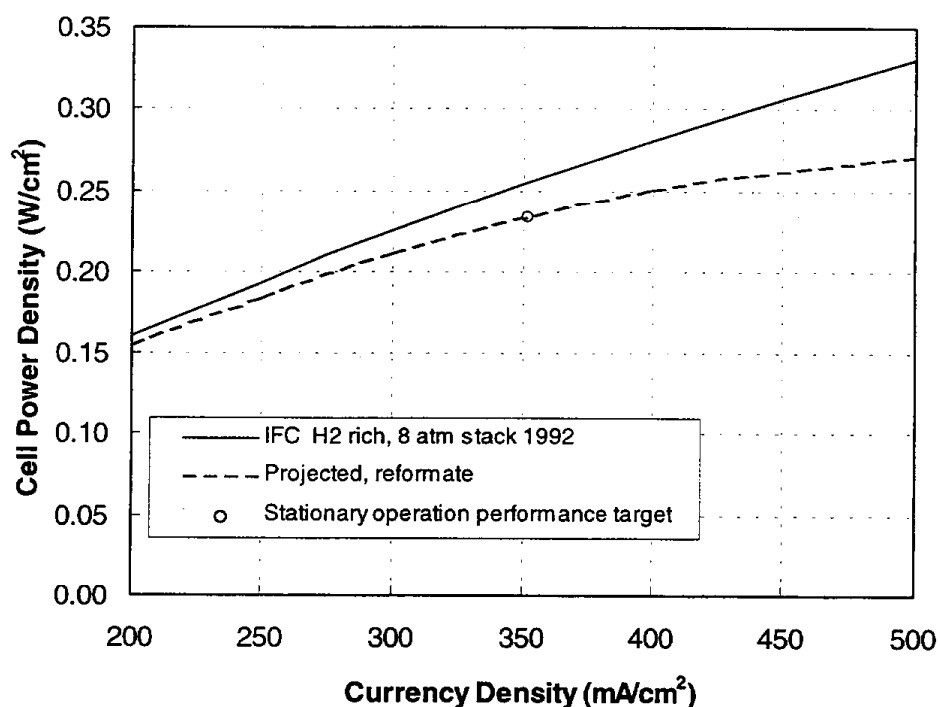


Figure 2-4. PAFC fuel cell stack power density, reformate operation

Table 2-2. Performance of ERC phosphoric acid fuel cell with reformer product gas (Ganser)

Feed Gas	Cell Voltage relative to H ₂ 60 % load	Cell Voltage relative to H ₂ 100 % load
100% H ₂	100%	100%
76.8% H ₂ , 23.2% CO ₂	97%	97%
75% H ₂ , 21% CO ₂ , 4% CO	95.7%	87%

The requirements of PAFC operation make them unsuitable for light-duty vehicle operation. The thermal management requirements of the fuel cell favor long periods of operation, whereas passenger cars are often driven briefly and parked for days. PAFCs could be suitable for transit buses which operate for up to 12 hours per day; however, these fuel cells will require specialized operating procedures. PAFCs cannot be started at room temperature but must be preheated to above 100°C before any current can be drawn. Furthermore, the PAFC must always be maintained under partial load to prevent the carbon support of the catalyst from oxidizing. PAFC systems on the buses, discussed in Section 4, require inert gas flooding to prevent oxidation from

atmospheric air. The fuel cell must also be trace heated to prevent expansion of the electrolyte upon solidification and subsequent damage to the fuel cell. These requirements can be incorporated into the operation of transit buses.

2.5 PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFC)

Beginning in the early 1960s, the General Electric Company developed a new type of fuel cell using a fluorocarbon ion exchange membrane as the electrolyte. The membrane was developed by DuPont and is sold under the name of Nafion. It consists of a Teflon matrix with side chains terminating in sulfuric acid groups. This proton exchange membrane may be viewed as a solid acid electrolyte. Because the electrolyte is acidic, carbon dioxide is not absorbed. This makes it possible to run a proton exchange membrane fuel cell on reformat derived hydrogen and air can be used as the oxidant source. This type of fuel cell was originally referred to as the Solid Polymer Electrolyte (SPE). Since the name has become a registered trademark for the Hamilton-Standard Division of the United Technologies Corporation, who bought the General Electric technology, it is generically called the Proton Exchange Membrane (PEM) fuel cell. The ion transport within the PEMFC, shown in Figure 2-5, is similar to that of the PAFC. The layout of the bipolar plate and membrane electrode assembly are also shown.

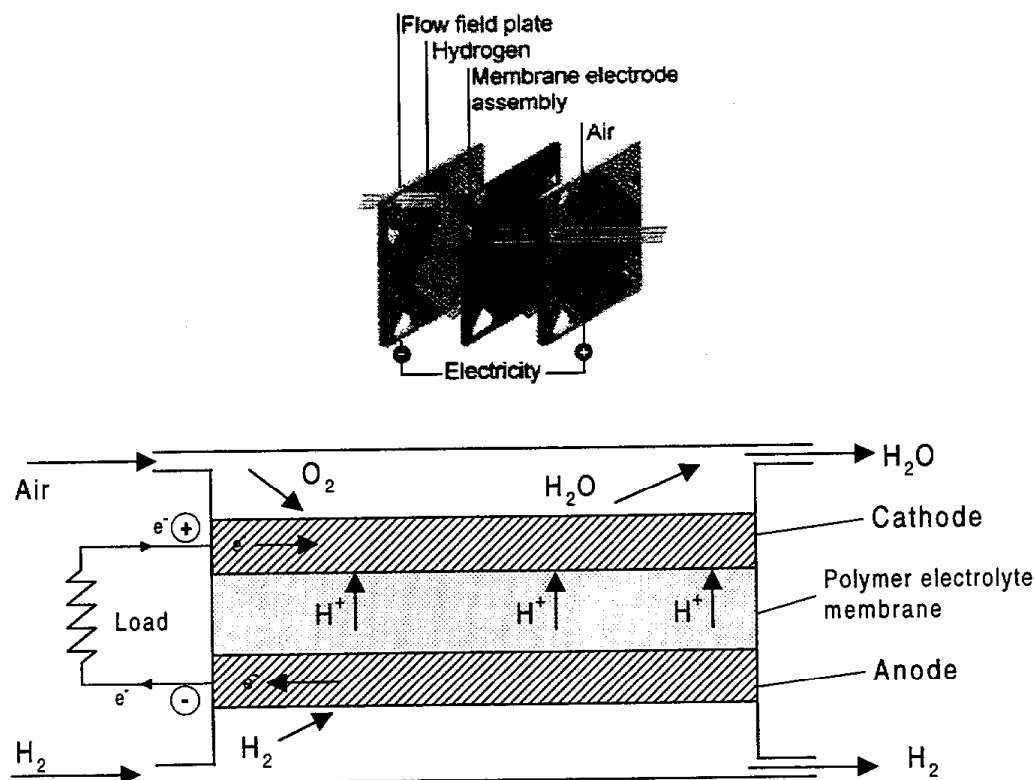


Figure 2-5. Operation of a proton exchange membrane fuel cell

The PEMFC offers several advantages over the PAFC for automotive applications. The paramount advantage is that it may be started-up from room temperature without the need for preheat. This eliminates both the delay and the complication associated with preheating systems. Unlike fuel cells using aqueous alkaline or acid solutions, the acid anion (SO_4^{2-}) is firmly bound to the solid fluorocarbon polymer. The acid ion cannot be transported by water, and therefore will not dissolve in water and corrode the electrodes or other fuel cell components. Additionally, the PEMFC does not create an acid hazard in the event of an accidental cell rupture. Similar to the PAFC, an extremely long (>10,000 h) electrode life is possible with PEMFCs. The solid polymer electrolyte is mechanically strong, and can be fabricated into thin sheets with low ionic resistance.

The PEMFC membrane must be saturated with water, since the H^+ proton will transport efficiently only if it is attached to water (forming a hydronium ion, H_3O^+) (Kordesch). Keeping the membrane saturated with water is accomplished by humidifying the hydrogen and oxidant streams. Failure to maintain water vapor partial pressure of at least 0.53 atm (400 mm Hg) results in a dehydration of the membrane, which leads to catastrophic increases in electrical resistance. Managing the water balance of a PEMFC system is a significant design consideration. Increasing the system pressure while maintaining the minimum partial pressure of water vapor reduces the overall water vapor concentration and increases the concentration of hydrogen which improves fuel cell performance. Maintaining a high water vapor partial pressure at the anode is further complicated by the fact that each hydronium ion migrating across the membrane and carrying the current is surrounded by 3 to 8 molecules of water as a hydration shell. This water must be continuously replenished. The need to keep the membrane from dehydrating and to supply a surplus of water to the anode increases the system complexity. PEMFCs that capture condensed water and recalculate it within the fuel cell for humidification are referred to as self-humidifying.

The humidification requirements of the PEMFC pose problems in extremely cold weather conditions. Water can accumulate in the fuel cell when the system is not operating and damage the fuel cell. PEMFCs may need to drain and purge water after shutdown in cold climates.

A significant advance in PEM technology was the development of a new membrane by Dow Chemical in the mid-eighties. Dow Chemical's membrane allows for much higher ion diffusion rates (without voltage loss) as compared with Nafion, thereby increasing current density. Ballard Power Systems, of Vancouver, British Columbia, developed PEMFCs using the Dow membrane. Fuel cells from several developers including Ballard, Energy Partners, Siemens, Plug Power and Los Alamos National Laboratory (LANL), have demonstrated remarkably high current densities as illustrated in Figure 2-6. Cell voltage outputs over 0.75V at 600 mA/cm² have been achieved. A key goal in fuel cell development is to maintain high efficiency without increasing the platinum content of the membrane. Higher catalyst loadings correspond to increased voltage output. The cost effectiveness of PEMFCs has also been improved with more efficient platinum deposition technologies pioneered by LANL. Voltage output with a platinum loading of 0.12 mg/cm² has been demonstrated to be almost as high as cells with a platinum loading of 8 mg/cm². Given the high cost per unit area of fluorocarbon membranes, a high current density improves the economics.

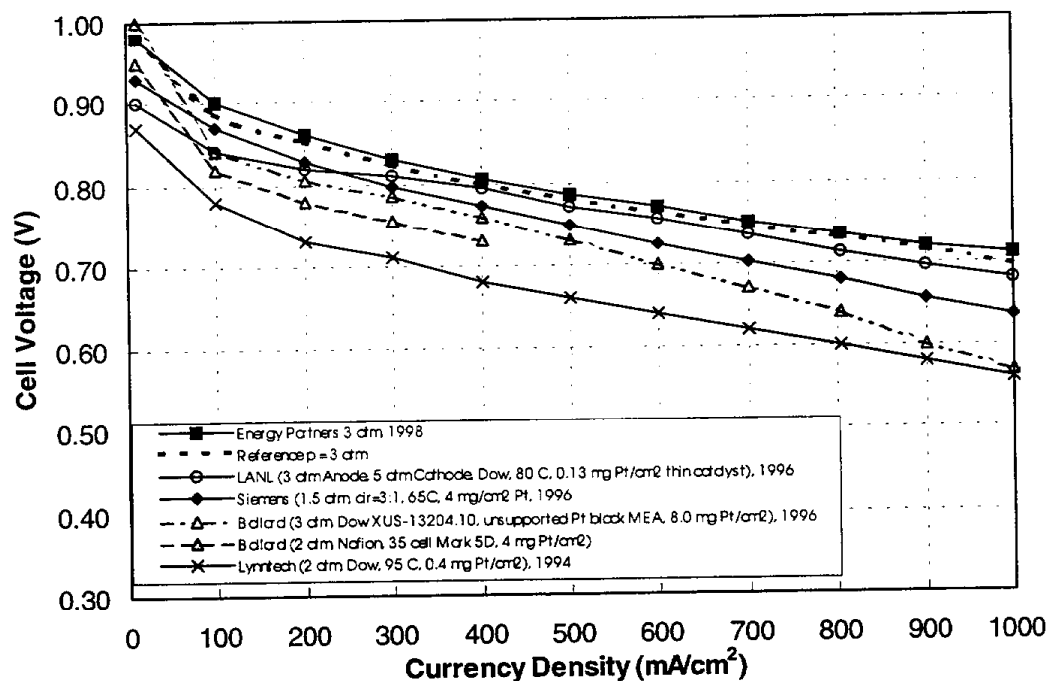


Figure 2-6. Cell voltage versus current density for various proton exchange membrane fuel cells

Ballard Power Systems is producing several PEMFC fuel cells shown in Figure 2-7. These include an integrated 250 kW natural gas reformer/PEMFC for stationary power generation and a 205 kW fuel cell for bus applications. They are also developing 30 to 50 kW systems for vehicle applications. Ballard fuel cells are being used by numerous automotive companies Daimler-Benz, Ford, General Motors (GM), Chrysler, Nissan, Honda, Volkswagen, and Volvo for vehicle development work as well as for stationary power generation.

Other PEMFC developers include IFC, Allied Signal, Siemens, Forschungszentrum (Research Center) Jülich (FZJ), H-Power, and Energy Partners. The IFC PEMFC will be used in a Ford prototype automobile. Allied Signal was one of the awardees of contracts by the DOE and SCAQMD for development of PEMFCs for vehicle applications. Allied Signal is designing a PEMFC system to meet the cost and performance goals of passenger cars (Rehg). The fuel cell stacks, shown in Figure 2-8, would be mounted along the bottom and centerline of an automobile. The fuel cell mounting includes plastic materials to reduce cost. The Allied Signal development effort includes designing the fuel cell for tolerance to CO in the feed gas stream. The goal of the development effort is to produce a 50 kW (net) PEMFC system that will operate on hydrogen from reformed gasoline, methanol, ethanol, or natural gas. The system will demonstrate the capability to achieve a fuel efficiency of 40 percent at 12.5 kW (cruising conditions).

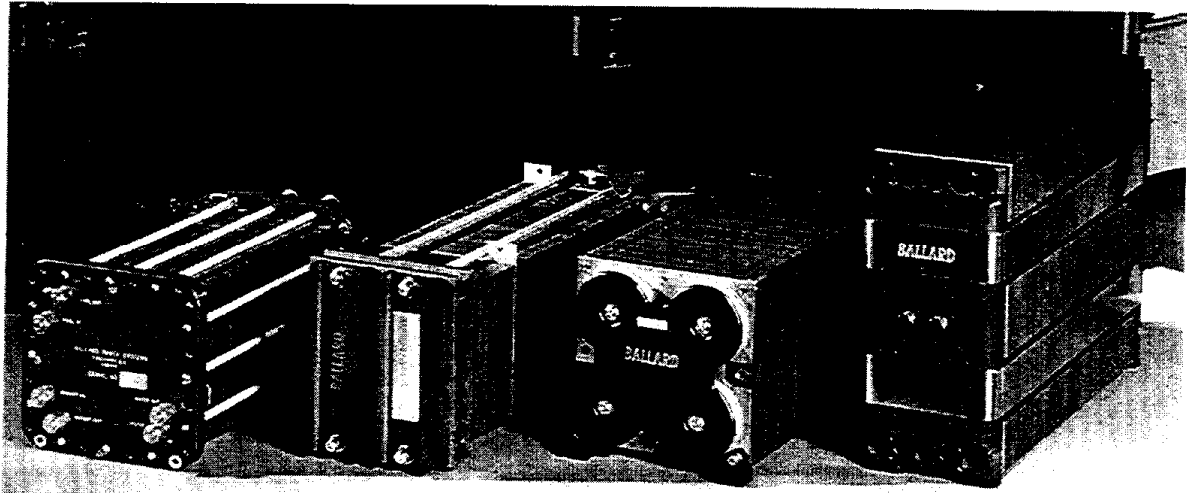


Figure 2-7. Ballard Power Systems manufactures several PEMFCs for vehicle and stationary applications (Photo courtesy of Ballard Power Systems)

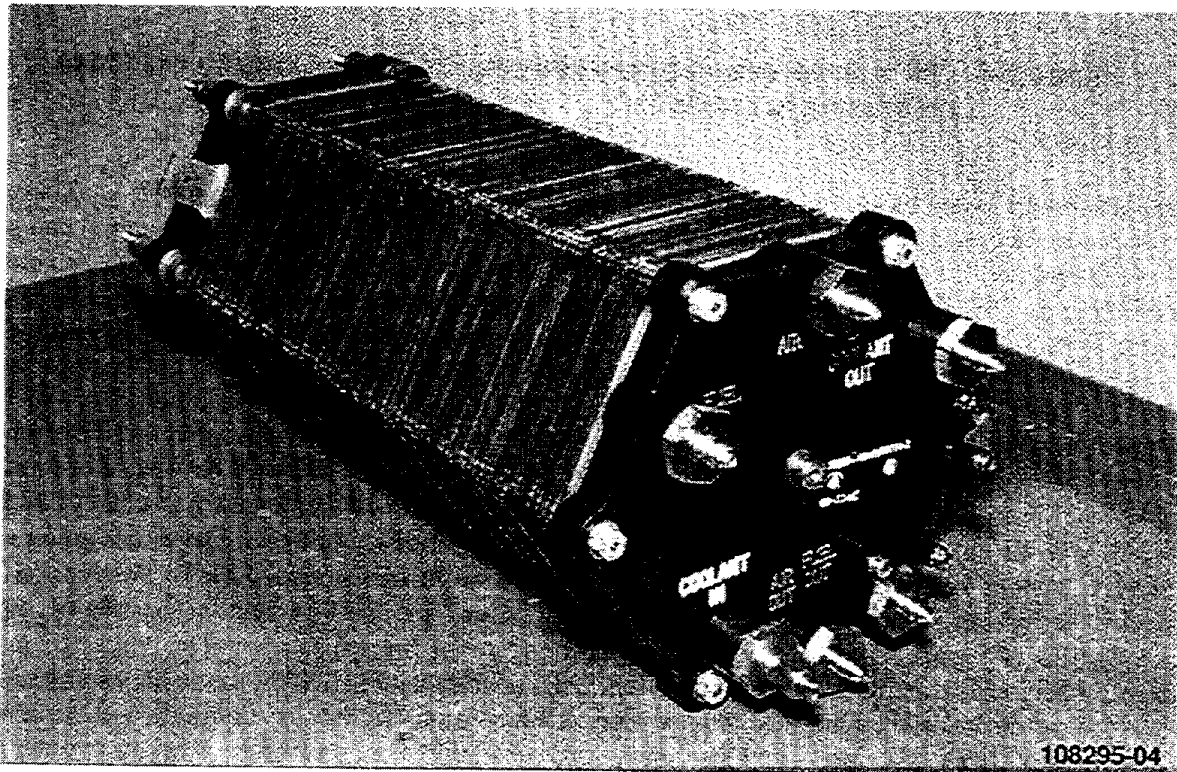


Figure 2-8. Allied Signal PEMFC for automotive applications

Figure 2-6 shows the performance for various PEMFCs operating on pure hydrogen and air. The voltage and resulting efficiency depend on a number of parameters including the following:

Fuel Cell Design Parameters

- Electrocatalyst loading
- Stack configuration, heat transfer, mass transfer
- Fuel cell temperature
- Stack geometry with full stack performance generally being lower than that of a single cell
- Membrane material

Fuel Cell System Parameters

- Operating temperature
- Cathode pressure and to a lesser extent anode pressure (typically between 1 and 4 atm)
- Deactivation (often short term) due to contaminants in the feed gas
- Anode and cathode stoichiometry (typically 1.2 for the anode and 2 for the cathode)
- Partial pressure of hydrogen and oxygen

The projected performance of PEMFC stacks operating on pure hydrogen at 1 and 3 atm¹ are shown in Figures 2-9 and 2-10. These performance curves are consistent with published values in the literature and provide the basis for predicting fuel cell performance with reformer feed. The improved cell output combined with the ability to deal with humidification make PEMFC operation at elevated pressures an attractive option. Operation at 3 atm reduces constraints for humidification and offers a good trade off between improvements in output and compression energy requirements. As discussed later, waste energy can be recovered from an integrated fuel cell/fuel processor system to provide the power needed for air compression.

2.5.1 PEMFC Performance for Vehicle Systems

Operating a fuel cell on-board a vehicle requires a source of hydrogen either from stored hydrogen or an on-board reformer. As discussed in Section 3, reformers will produce gas streams that contain diluents such as CO₂ and nitrogen as well as contaminants such as CO and ammonia.

¹ Values refer to absolute pressure in this study. 1 atm is ambient pressure.

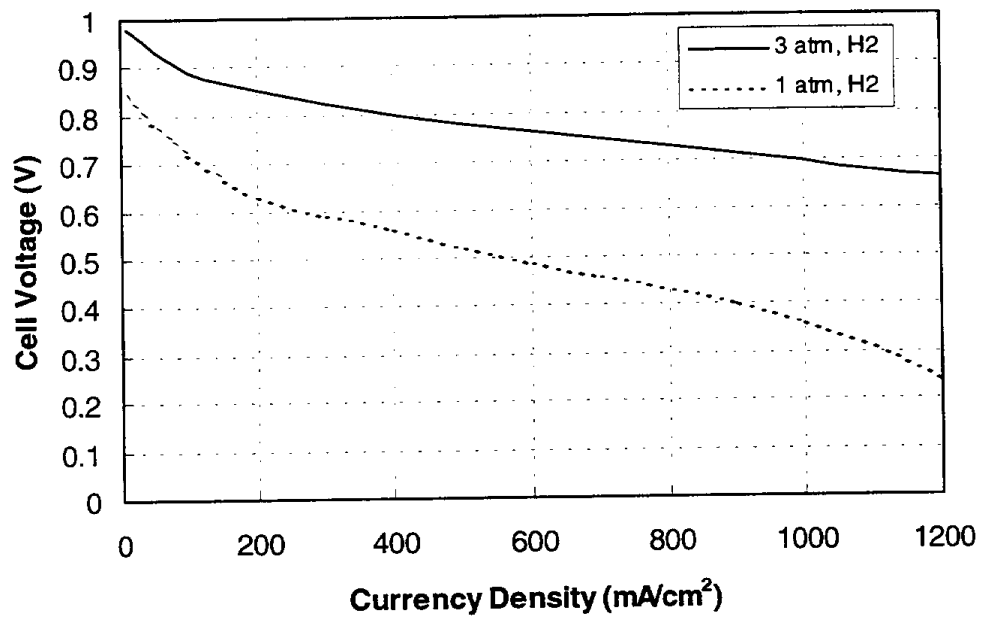


Figure 2-9. PEM fuel cell stack performance, hydrogen operation

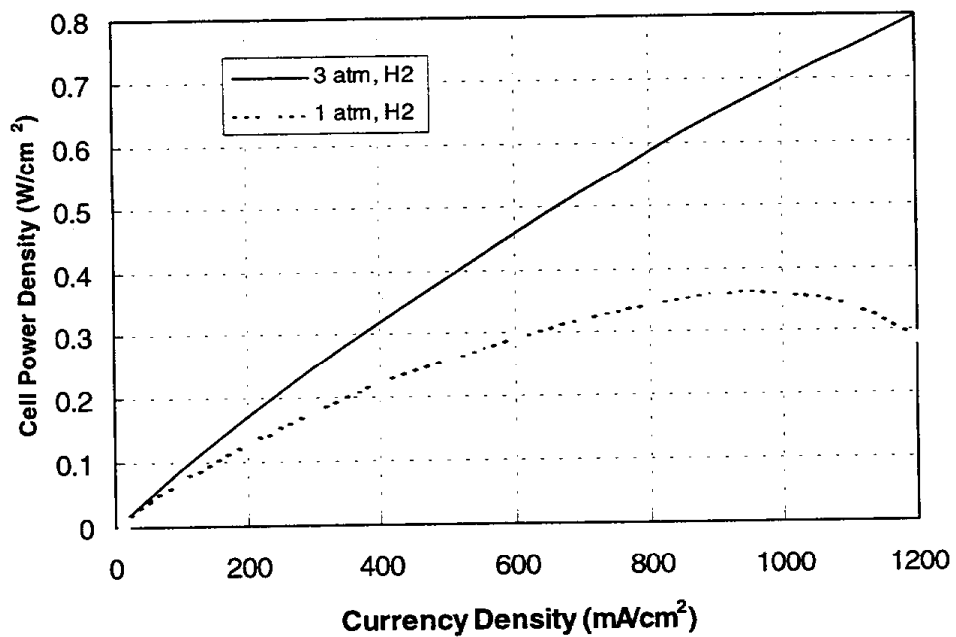


Figure 2-10. PEM fuel cell stack power density, hydrogen operation

Operating temperatures of proton exchange membranes are limited by the onset of membrane dehydration to a maximum of 80 to 100°C, depending on operating pressure. The negative consequence of having a relatively low operating temperature is extreme sensitivity of the electrocatalyst to carbon monoxide poisoning. At 80°C the allowable concentration of CO in the fuel is only a few parts per million (Krumpelt). Accordingly, PEM cells that are fueled by reformat gas must include a CO oxidizer downstream of the reformer or other CO removal techniques.

CO blocks the reaction sites on the cell and limits the cell voltage. The effect of CO is not permanent once CO is removed. Consequently, research has focused on both CO removal systems and improving the PEM tolerance to CO. Table 2-3 shows the effect of contaminants on fuel cell operation from various references. PEM performance with a platinum/ruthenium electrocatalyst show marked improvement over a PEM with a platinum only electrocatalyst.

Table 2-3. Reduction in PEM performance with contaminants

Contaminant in Hydrogen Feed, Concentration	Change in Stack Voltage	Baseline Fuel Cell Operating Conditions	Reference
CO 5 ppm CO 10 ppm with PEMFC Pt catalyst	-0.11 mV -0.23 mV	600 mA/cm ² 0.57 V 3 atm	Lemons 1990
NO ₂ 10 ppm NO 10 ppm SO ₂ 10 ppm SO ₂ NH ₃ 10 ppm Toluene 10 ppm Methane 10 ppm with PEMFC Pt catalyst	-45 mV ~ 0 mV -5 mV -20 mV -5 mV -4 mV ~0	150 mA/cm ² 0.68V/cell 20 Cell stack	Sanyo 1996
CO 100 ppm with PEMFC Pt/Ru catalyst	~0 mV -20 mV -50 mV	400 mA/cm ² 600 mA/ cm ² 800 mA/cm ²	Kawatsu 1996
CO 100 ppm with PEMFC Pt catalyst	-200 mV	200 mA/cm ²	Kawatsu 1996
CO 100 ppm with PEMFC Pt/Ru catalyst	Achieved 300 hours operation at LANL		Chalk 1996

Figures 2-11 and 2-12 show projections of PEMFC stack operation at 3 atm with pure hydrogen, reformat from a steam reformer, and reformation from a partial oxidation reformer system. The effect of CO and hydrocarbon contamination is determined from published literature. The reduction in cell voltage output from dilution is predicted from theoretical relationships. The predicted curves for reformat operation are consistent with published values. The POX output is likely to contain more trace contaminants and will also have a lower hydrogen concentration than that of a steam reformer output. The cell voltage drop for the steam reformer is based on 20 ppm CO and the effect of dilution. The effect of dilution is also taken into account for the POX reformat. The cell voltage reduction is based on 20 ppm CO and additional 5mV to take into account traces of hydrocarbons. The net voltage output from a PEMFC exceeds the goals by Ford for reformer systems (0.6 V at 500 mA/cm²).

Low temperature operation, high power density, and relatively high efficiency make PEMFCs good candidates for vehicle applications. PEMFCs are sensitive to CO which places constraints on the fuel processor system. Nevertheless, this fuel cell technology is the leading candidate for commercial vehicle applications.

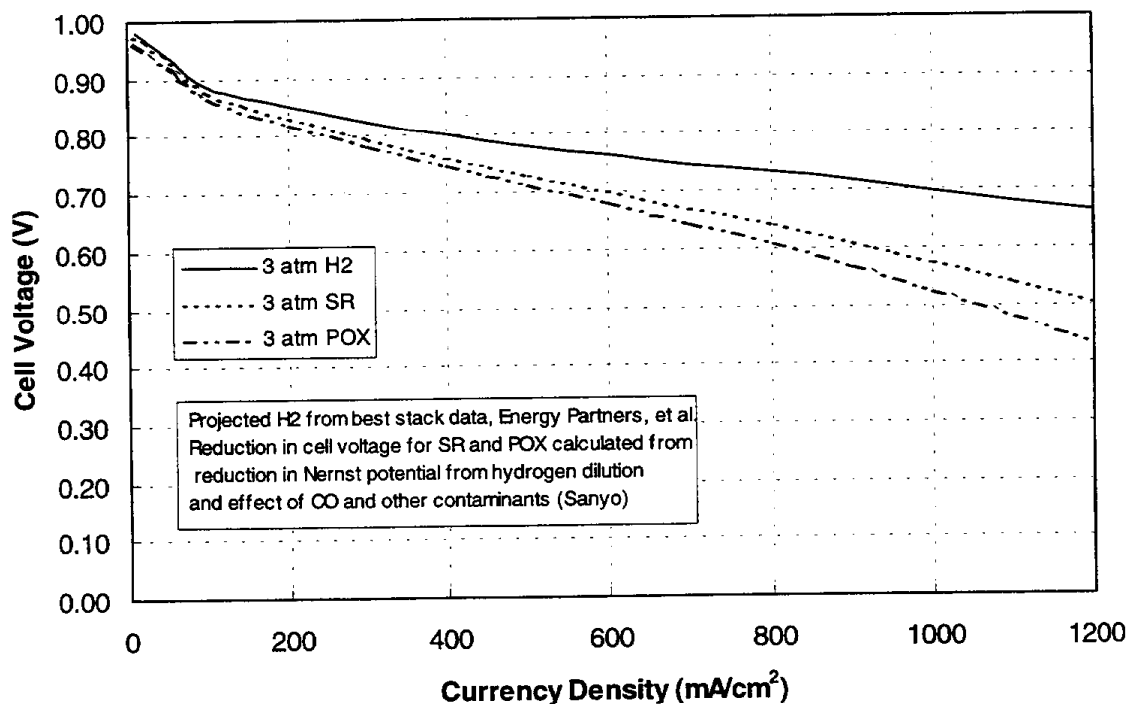


Figure 2-11. PEMFC stack performance, hydrogen and reformat operation, 3 atm

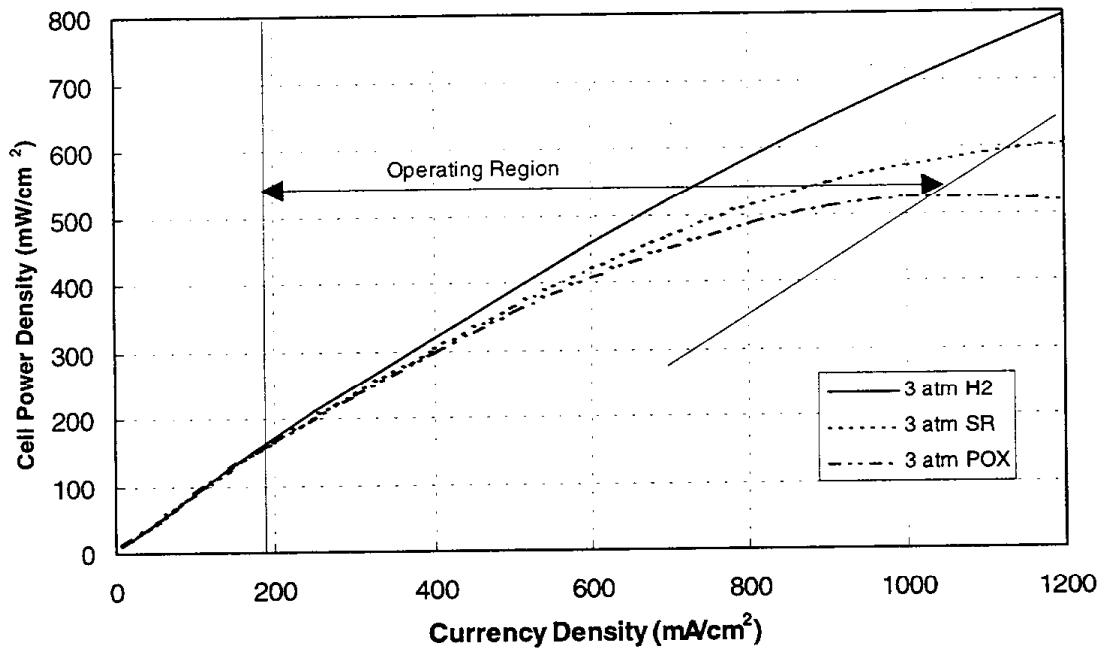
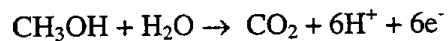


Figure 2-12. PEMFC stack power density, hydrogen and reformat operation, 3 atm

2.6 DIRECT METHANOL FUEL CELL (DMFC)

The DMFC has features which make it attractive for vehicle use. It operates on a liquid fuel and does not require a fuel processor. The DMFC operates on methanol in a water solution. The DMFC consists of a solid polymer membrane (PEM) with a methanol/water mixture on the anode side and air on the cathode. The oxidation of methanol proceeds according to the following reaction:



with the transport of protons occurring in the same manner as that in a PEMFC. Figure 2-13 illustrates the operation of the DMFC. The methanol is circulated in a 0.5M (molar) solution (3 percent) in water. In a DMFC system, the water solution would be circulated with fresh water and methanol replacing the depleted components. Some methanol migrates across the PEM. All of the carry over methanol appears to be converted to CO_2 on the cathode which results in a zero emission system. Some of the methanol could be oxidized to species other than CO_2 such as CO or formaldehyde; however, no such emissions have been observed in the limited testing that has been conducted by JPL (Halpert 1997a). The only potential source of emissions from the DMFC are vapor from the methanol water mixture. The DMFC has the advantage of not requiring

humidification and complex cooling systems. The carrier water serves as a fuel cell stack coolant. Methanol is also a liquid fuel and does not need to be reformed for use in the DMFC.

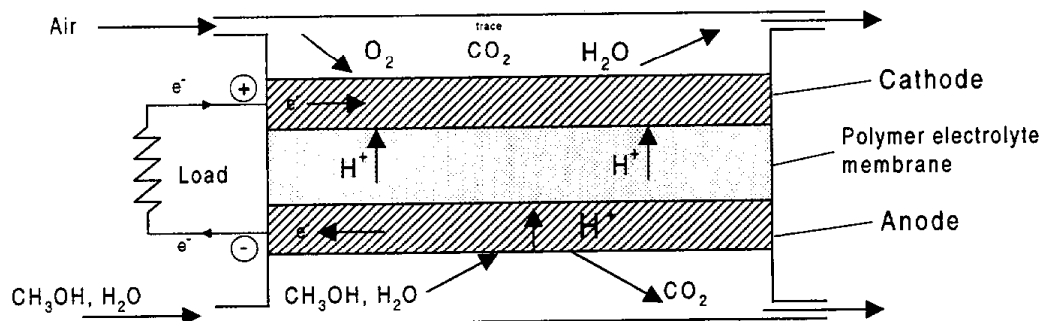


Figure 2-13. Operation of a direct methanol fuel cell

The Jet Propulsion Laboratory (JPL) has made considerable advances with the DMFC. Starting in 1992, JPL achieved a substantial increase in cell voltage output at higher current densities. This breakthrough was made possible by improvements in the membrane catalyst composition, electrode structure, interface between the membrane and electrode, and catalyst processing. In 1997, the size of developmental DMFC stacks was in the range of several hundred Watts. These developments are likely over five years away from producing a fuel cell stack that could power a light-duty vehicle.

Early cells produced low voltages at low power densities. In late 1992, JPL was able to achieve a substantial increase in cell performance, delivering an output of 0.5 V at 0.3 A/cm². The performance of different DMFC configurations are shown in Figure 2-14. The JPL DMFC operates at temperatures of 60 to 90°C and both the anode and cathode are pressurized to 2.4 atm. Early configurations had a methanol carry over of 20 percent. JPL projects that the carry over can be reduced to 5 percent. Cell outputs of 0.6 V are also projected. These improvements would result in an overall efficiency improvement from 34 percent to 47 percent (Halpert, 1997). DMFCs are currently smaller than 100 W. A significant scale up effort is required to produce cells that can operate in the 20 to 50 kW range required for vehicles. A near term objective is to produce a 5 kW system for small mobile power applications. Issues of fuel purity affecting catalyst poisoning and the build up of contaminants in the water solution also need to be addressed. The fate of higher order alcohols and hydrocarbons in the methanol needs to be investigated also.

DMFC development is being pursued at Los Alamos National Laboratory, Jet Propulsion Laboratory (JPL), FZJ, and Siemens. IFC has also been active in DMFC development. Their work for the department of defense contributed to reducing methanol carry over.

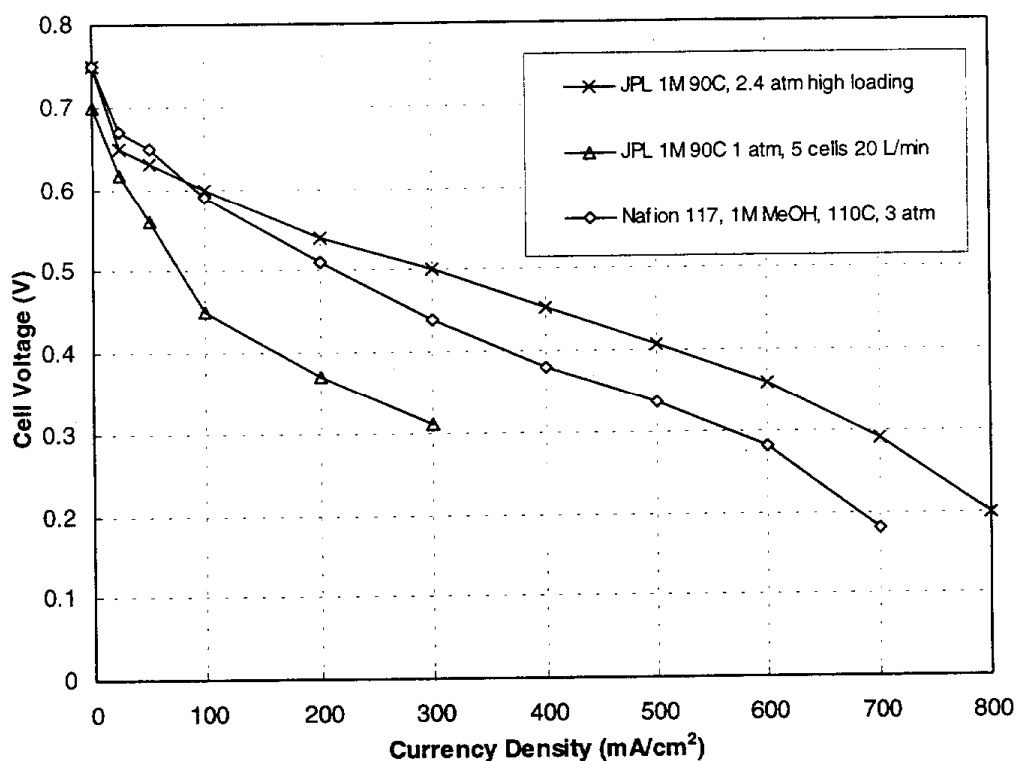
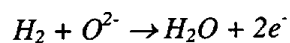


Figure 2-14. Performance of various DMFC configurations

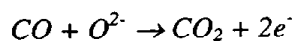
Figures 2-15 and 2-16 show the projected output for DMFC stack systems. The DMFC operates at a lower power density than the PEMFC or PAFC. However, since methanol is transported in the liquid phase, the DMFC has the potential for efficient packaging.

2.7 SOLID OXIDE FUEL CELL (SOFC)

Solid oxide fuel cells operate at very high temperatures. This feature allows CO as well as hydrogen to be converted to power in an electrochemical reaction. As illustrated in Figure 2-17, the reaction mechanisms for the SOFC are different than those previously discussed. Ionized oxygen travels across a ceramic membrane where it reacts with any material that can be oxidized. An SOFC can convert a wide variety of fuels. While carbon and sulfur are poisons to the low temperature platinum electrodes of PEMFCs, an SOFC consumes CO and sulfur as fuel. The anode reactions are the following:



and



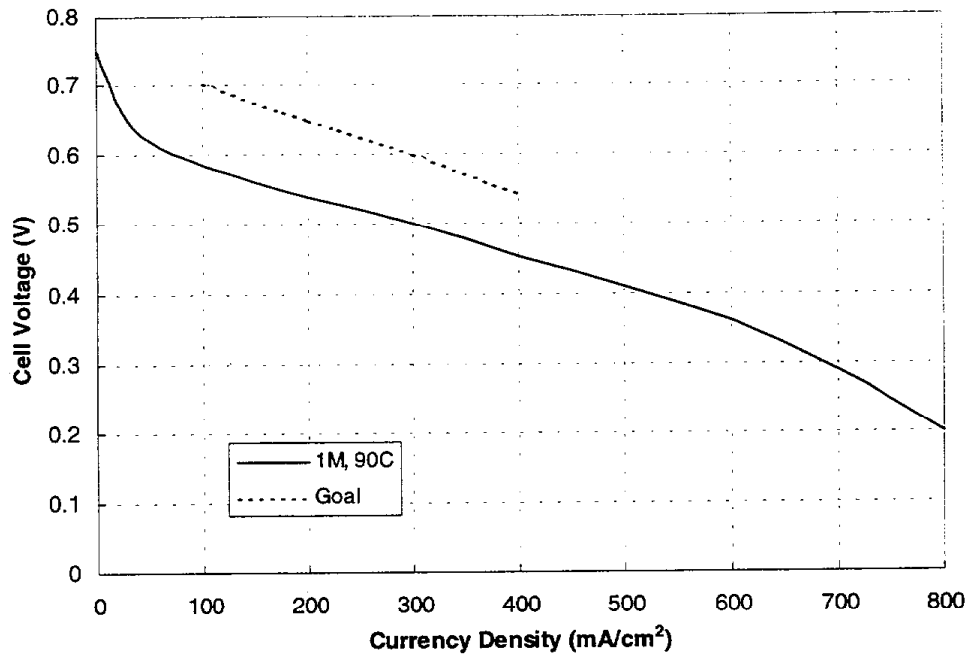


Figure 2-15. Projected DMFC stack performance (Halpert)

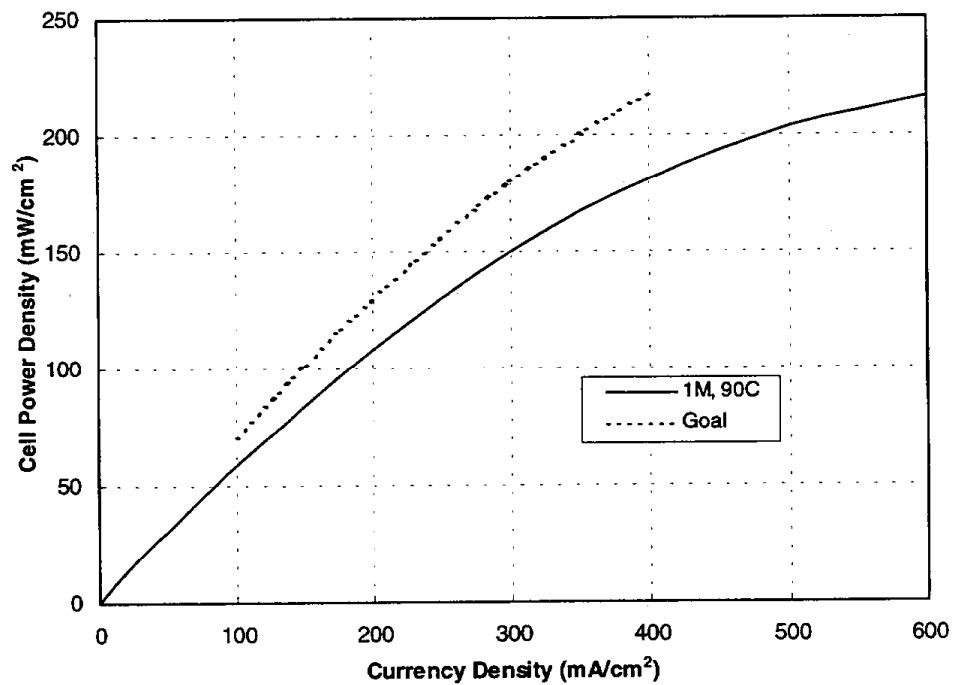


Figure 2-16. Projected DMFC stack power density (Halpert)

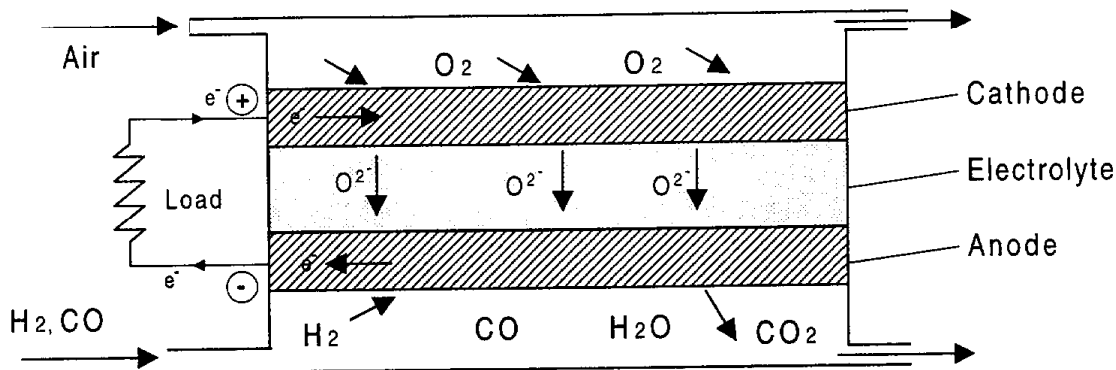


Figure 2-17. Operation of a solid oxide fuel cell

Several SOFC designs are under development. These include tubular, planar, and monolithic configurations. All SOFC technologies require more development before being viable for full scale applications.

Westinghouse is developing a design where air flows inside a ceramic tube and the anode gas, typically methane flows over the outside of the tube. One configuration consists of 1.5m long 12 mm diameter tubes which are mounted vertically in a tube sheet. Oxygen migrates through the tube and reforming occurs in the first section of the tube. The fuel cell reaction occurs further along the tube. One disadvantage of this configuration is that the endothermic reaction for reforming occurs on one end of the tube while the exothermic fuel cell reaction occurs on the other end which results in a thermal gradient and cracking. Further development is aimed at improving the strength of the ceramic materials. The Westinghouse SOFC generators are reported to operate without performance problems when cycled from 1000°C to room temperature (Westinghouse 1997). The tubular SOFCs are intended for power plant applications.

Planar and monolithic SOFCs could potentially be used for vehicle applications. These fuel cells consist of a sandwich of porous ceramic and nickel. Allied Signal is developing a monolithic design which consists of corrugated layers. Ztek, Ceramtec, the Electric Power Research Institute (EPRI), and others are developing systems based on a stack of ceramic discs.

SOFCs are a solid state construction constructed of yttria-stabilized zirconia (YSZ) electrolytes. A key issue with SOFCs is cracking of seals and bonding of components which must operate at high temperatures. An alternative planar SOFC design employs modified ceramic electrodes that are particularly porous to fuel and oxidant (EPRI). These cells can be stacked together rather than bonded. Consequently, electrolytes, electrodes, and separator plates can be cut from sheet materials at low cost.

The high operating temperatures for SOFCs reduce the potential efficiency. The theoretical open circuit voltage is lower than that of a PAFC or MCFC; however, the higher operating temperatures help reduce ohmic losses (polarization). The waste heat from an SOFC can also be

recovered to generate additional work. Since the exit temperature is much higher than other fuel cells, there is more flexibility for powering a turbine or generating steam for stationary power generation. Figure 2-18 shows the performance of SOFCs operating at 1000 and 800°C. The University of Utah fuel cell represents a more conservative design with the aim of improving system reliability. For a given SOFC configuration, the open circuit voltage is generally higher at lower temperatures but the drop off in temperature is not so steep for lower temperatures. The data shown in Figure 2-18 represents different designs so factors other than temperature are affecting the fuel cell performance. Operating the fuel cell at lower temperatures eliminates material problems but also results in a reduction in a drop in voltage. This low temperature configuration may be suitable for vehicle applications. The on and off operation of passenger cars presents a difficult operating profile for SOFCs due to the large thermal cycling. SOFCs might be more suitable for transit bus applications where the unit could operate at a steady load. A small experimental SOFC buggy which operates on diesel fuel is being tested at Keele University in England. Development of an SOFC for commercial vehicles is well over five years away.

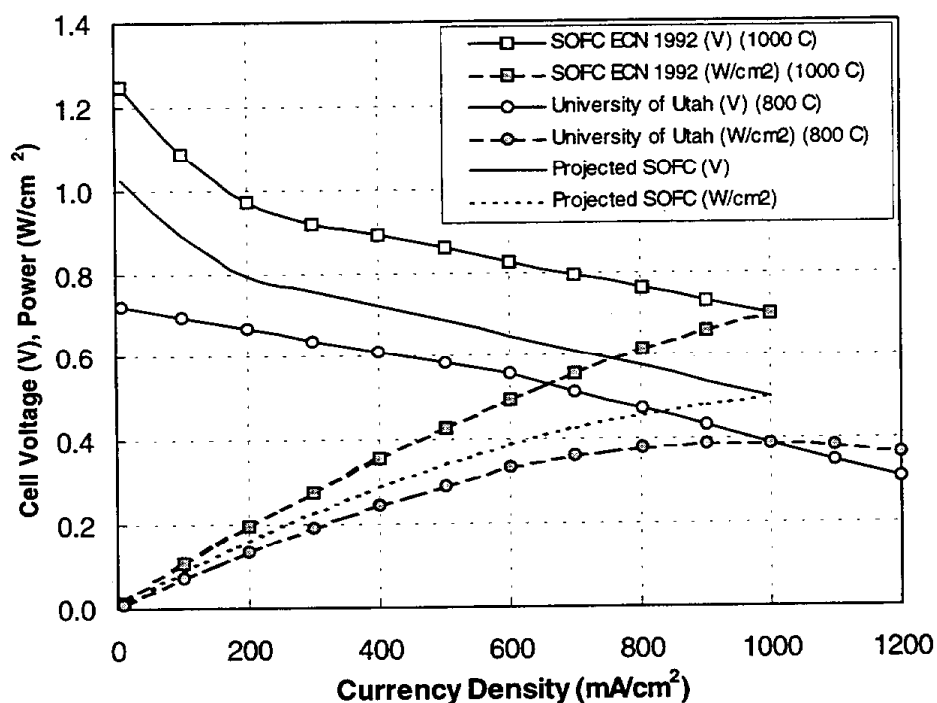


Figure 2-18. Solid oxide fuel cell performance

2.8 MOLTEN CARBONATE FUEL CELLS (MCFC)

Molten carbonate fuel cells (MCFCs) operate at a temperature between 600 and 650°C. The fuel cell is based on a reaction with carbonate ions travel through a molten electrolyte as shown in Figure 2-19. The anode reaction is the following:

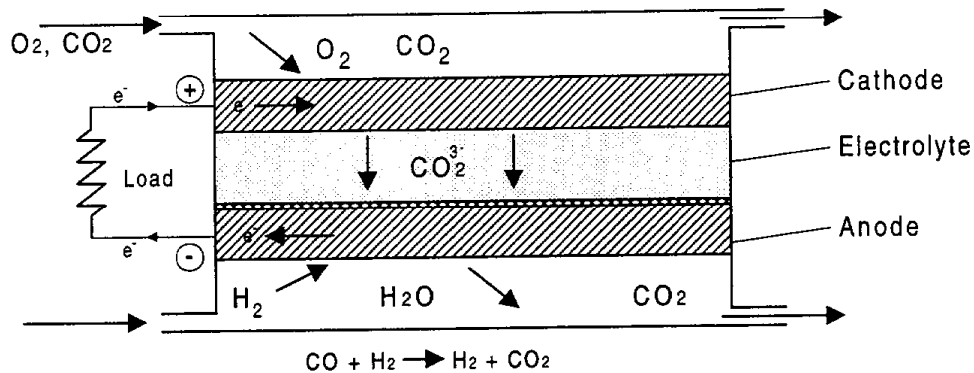
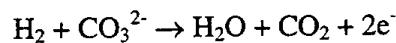


Figure 2-19. Operation of a molten carbonate fuel cell



The lower operating temperatures for MCFC increase their potential efficiency. The open circuit voltage is higher than that of a PAFC or SOFC which results in a very high thermal efficiency. The performance of and MCFC is shown in Figure 2-20.

The thermal management requirements of MCFCs combined with the complexity of the balance of system make them unsuitable for vehicle applications. A MCFC could conceivably be used to power a locomotive, however, MCFCs have not achieved the level of commercial development as PAFCs and PEMFCs so such a system would require an extensive development effort

2.9 VEHICLE PROPULSION OPTIONS

Among the fuel cell options, PEMFCs are the leaders for near term commercialization. They have the advantages of low temperature operation, higher power density than PAFCs, and ability to operate over a range of loads without adverse consequences. PEMFCs have the significant disadvantage of being sensitive to CO in the gas stream. The higher operating temperatures of PAFCs excludes them as candidates for light-duty vehicle applications. The energy required for start up for short driving trips combined with the thermal packaging requirements exclude their use in light-duty vehicles but can be packaged on heavy-duty vehicles. DMFCs are attractive since they do not require a complex fuel processing system and can operate directly on methanol. DMFCs require significant development before they can be packaged in a vehicle application. SOFCs achieve very high thermal efficiencies. They operate at high temperatures and can be combined with a turbine for hybrid power generation. The high operating temperature make

them less attractive for light-duty applications. SOFCs which are constructed with ceramics, may not be able to withstand the vibrations from on-road operation. SOFCs also require a significant development effort before they can be packaged. The high temperature and complexity of MCFC power plants make them unsuitable for vehicle applications. MCFCs could possibly be packaged on locomotives however, they require more development before they are used on a large scale for stationary power generation.

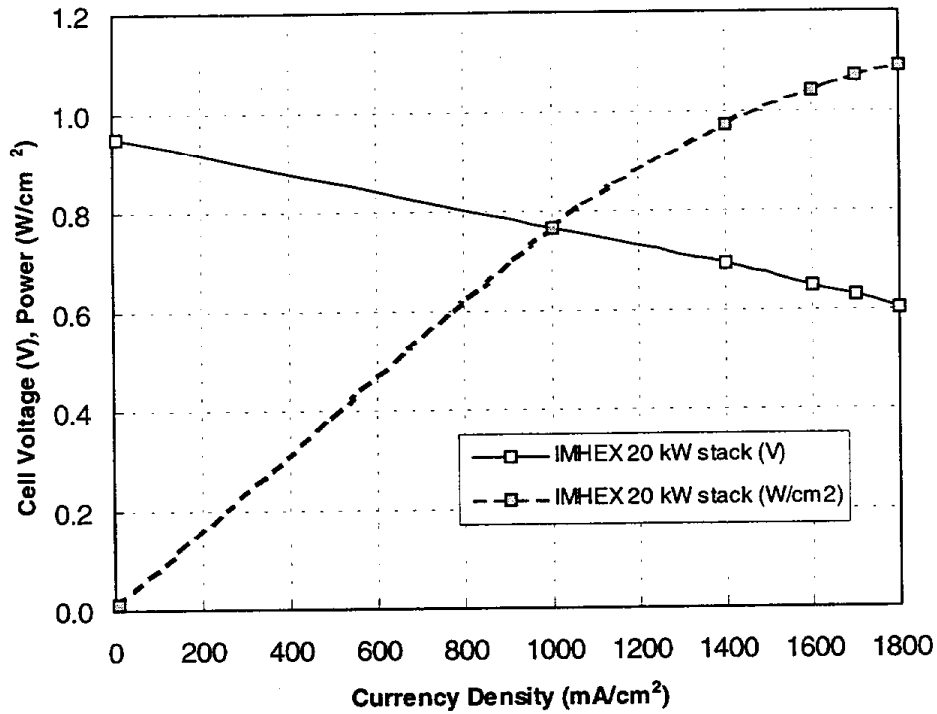


Figure 2-20. Performance of a molten carbonate fuel cell

3. REFORMER TECHNICAL EVALUATION

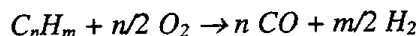
The production, distribution, lack of fueling infrastructure, and the difficulties in storing sufficient quantities of hydrogen onboard a vehicle or near a stationary facility are all obstacles that make the mass introduction of hydrogen-powered fuel cells difficult. As a result, considerable research has been directed towards developing technologies for the on-site or on-vehicle production of hydrogen. The addition of a fuel processor to generate hydrogen from existing liquid hydrocarbon fuels is an attractive alternative to hydrogen storage. Liquid hydrocarbon fuels have high energy densities, established storage and handling characteristics, and existing or easier to establish fueling infrastructures. The constraints imposed by vehicle operation and the fuel cell, however, need to be incorporated into the design of on-board fuel processors.

Hydrogen has been produced from natural gas and other hydrocarbon fuels in methanol and chemical plants and in oil refineries for decades. Two approaches are used for commercial hydrogen production.

- Steam Reforming (SR)
- Partial Oxidation (POX)

In commercial steam reforming facilities, a feedstock such as natural gas reacts with steam over a nickel catalyst to produce hydrogen, CO, and CO₂. With natural gas, the reaction temperature is about 800°C and waste process heat is used for preheating fuel and generating steam for process feed and power generation. Because the reforming reaction is endothermic, a portion of the reformat is generally burned to produce an external heat source for the reaction energy.

POX systems use oxygen to react with a feedstock to produce hydrogen and CO. The oxidation of hydrocarbons proceeds according to the following reaction:



In the case of methane:



Industrial POX reactors operate at pressures ranging from 40 to 80 atm. Reaction temperatures range from 1200 to 1500°C, much higher than those of steam reformers. The POX reaction is exothermic, and the reaction takes place within a reaction chamber. Because the heat of reaction

is generated from the combustion of the feedstock, an additional heat source is not required. This fact makes POX reactors compact. The POX approach is also termed a reforming technology because most POX systems include the addition of steam to provide some degree of reforming with the reaction of oxygen and fuel. The operating temperatures of POX systems are high, however, so they require careful control of air preheating to protect the materials.

Low temperature methanol steam reformers can also be built sufficiently compact for passenger cars and produce a quality of the hydrogen. However, methanol is not widely available at vehicle fueling stations at this time.

Combined steam reforming and POX systems have also been built for hydrogen production. This approach is referred to as autothermal reforming because the POX reaction generates sufficient energy for the endothermic steam reforming reaction. An autothermal reformer (ATR) uses a catalyst for steam reforming at a temperature of approximately 800°C. The addition of steam to a non catalytic POX process is also feasible. The ATR approach combines the benefits of the POX system with a degree of steam reforming.

ATRs are similar in performance to POX reactors; however, they are more sensitive to sulfur in the fuel, and expensive catalyst are needed. Because an ATR operates at lower temperatures, some material problems are eliminated. The lower operating temperature can lead to reduced fuel conversion or residual methane in the process gas, a downstream reforming step can convert the methane to CO and hydrogen. ATRs can also be optimized to operate on methanol at low temperatures where fuel conversion is not compromised.

Several groups are actively involved in the development of fuel processor systems for fuel cell vehicles. Table 3-1 identifies fuel processors that have been built on a scale suitable for vehicle applications with the goal of scale up to vehicle operation.

The following sections discuss steam reforming and POX approaches for on-board hydrogen production. Section 3.1 summarizes properties of fuels that are applicable to reforming in vehicles. Section 3.2 presents the steam reformer (SR) technical evaluation. Section 3.3 describes the POX technology. Section 3.4 provides information on gas cleanup requirements and techniques. Section 3.5 briefly describes other reformer systems, and Section 3.6 provides data on peripheral system components.

3.1 FUELS

In theory, any hydrocarbon fuel can be used as a feedstock for hydrogen production, but fuel properties affect the efficiency and performance of a fuel cell reformer system. The thermodynamic properties of the fuel determine the reformer yield and impurities result in trace gas contaminants in the reformat. The physical properties of fuels also affect the mechanical aspects of fuel handling, such as injector performance, and the reaction rates in the reformer. Table 3-2 shows the properties of a variety of pure compounds and fuels that are available in California. Real fuels vary in composition. The values shown in this table are based on a consistent combination of heating value and compositional measurements for fuels sold in California.

Table 3-1. Fuel reformer development activities

Organization	Technology	Fuel (s)	Scale (electric power)
Delphi, GM, Opel	Low temperature steam reforming	Methanol	On-vehicle (50 kW)
Fuji	Low temperature steam reforming	Methanol	On-vehicle (57 kW)
Ballard	Low temperature steam reforming	Methanol Methanol	Transit bus (100 kW) Submarine power generator
International Fuel Cells	High temperature steam reforming	Natural gas, LPG, Methanol	PC25 fuel cell (200 kW) Transit bus (100 kW)
Halder Topsøe, Siemens, KFA	Low temperature steam reforming	Methanol	Laboratory burner Reformer Laboratory membrane Joule II, On-vehicle (30 kW)
Argonne National Lab	Catalytic partial oxidation	Methanol, Ethanol, Gasoline, Natural gas	10 kW
A. D. Little	Catalytic partial oxidation, POX	Ethanol, Gasoline, JP-8	Five units, various applications 50 kW
Hydrogen Burner Technology	POX	Natural gas, LPG, Methanol, Gasoline, Diesel	POX Industrial hydrogen production (50 kW, 300 kW) Prototype for vehicle (50 kW)
Johnson Matthey	Hot Spot™ partial oxidation	Methanol	Designed for industrial hydrogen and vehicles (10 kW) able to be clustered

Table 3-2. Fuel properties

Fuel ¹	Formula	H/C	MW (g/mole)	Density ² (kg/m ³)	RVP (kPa)	HHV (MJ/kg)	LHV (MJ/kg)	Heat of Formation (kJ/mol)	C _p (kJ/kg°C)	C _v (kJ/kg°C)	Heat of vaporization (kJ/kg)
Gasoline	C _{8.95} H _{13.26} (l)	2.024	92.03	719	58	48.4	44.7	-72.0	~ 1.67	2.4	305
RFG	C _{8.69} H _{13.65} O _{0.121} (l)	2.041	96.05	719	47	47.2	43.7	-85.0	~ 1.67	2.4	305
Diesel No. 2	C _{12.4} H _{21.15} (l)	1.706	170.25	863	0.21	46.5	42.6	-193.3	~ 1.67	1.9	270
Diesel No. 1	C _{11.1} H _{20.27} (l)	1.826	153.74	827	0.21	45.5	43.6	-116.1	~ 1.67	1.9	270
Iso-octane	C ₈ H ₁₈ (l)	2.25	114.22	710	19	47.8	44.3	-260.0	1.67	2.15	308
LPG	C ₃ H _{7.86} (l)	2.626	43.97	504	930	50.2	46.0	-111.8	2.5	1.6	426
Propane	C ₃ H ₈ (l)	2.667	44.09	510	930	50.4	46.4	-103.8	2.5	1.6	426
Natural Gas	CH _{3.85} O _{0.019} N _{0.031} (g)	3.85	16.20	0.79	—	52.3	47.2	-94.5	~ 2.2	—	—
Methane	CH ₄ (g)	4	16.04	0.78	—	55.6	50.0	-74.9	2.19	—	—
Methanol	CH ₃ OH (l)	4	32.04	792	32	22.8	20.0	-236.5	1.7	2.6	1100
Ethanol	C ₂ H ₅ OH (l)	3	46.07	785	15.9	29.8	27.0	-270.1	1.9	2.5	840
Hydrogen	H ₂ (g)	—	2.02	0.098	—	142.1	119.9	0.0	14.3	—	—

¹ Heating values and heats of formation are for liquids except for natural gas, methane, and hydrogen.

² Density for natural gas, methane, and hydrogen are for gases at 1 atm, 25°C.

Reference: Lindeburg 1984, CRC Handbook of chemistry and physics 1987, Gieck 1989, Kanury, Unnasch, 1996, Heywood, 1988.

Some of the fuel properties listed in Table 3-2 warrant further explanation. Gasoline refers to regular unleaded gasoline sold in California prior to 1996. The vapor pressure corresponds to a summer blend (8.4 psi Reid Vapor Pressure (RVP)). The other fuel properties are consistent with this vapor pressure. Gasoline with a different RVP would likely vary in H/C ratio, heating value, and heat of formation because the fuel's vapor pressure can be adjusted by adding or removing butane. The average molecular weight and H/C ratio of butane are sufficiently different than those of gasoline so the properties would be different if the butane content were varied. Therefore, these properties need to be recalculated if the reader is interested in evaluating winter formulation fuels. Reformulated gasoline (RFG) refers to phase 2 reformulated gasoline that is sold in California during the summer. This fuel has a lower RVP (7 psi for summer RFG) than conventional gasoline and also contains 2 weight percent oxygen. The olefin and aromatic content of the fuel are lower which is reflected by the H/C ratio.

The average molecular weight of gasoline, RFG, liquefied petroleum gas (LPG), and natural gas were calculated from speciated data. The chemical formula of the fuels is consistent with the average molecular weight. For example, with gasoline, $6.55 \times 12.01 + 13.26 \times 1.07 = 96$. The heat of formation is necessary when predicting the operating temperature of POX reactors and burners. The heats of formation for common fuels (corresponding to the compositions of real fuels) are not readily available, but were calculated from the lower heating value and the heats of formation from the product H_2O and CO_2 . For example, in the case of gasoline, $C_{6.55}H_{13.26}$ results in the production of 6.55 CO_2 and 6.63 H_2O .

Thus the heat of formation of gasoline is determined from:

$$\Delta H_f = -LHV + n H_f CO_2 + m H_f H_2O$$

$$\Delta H_f = 981.9 + 6.55(-94.05) + 13.25/2 (-57.79) \text{ kcal/mol} = -17 \text{ kcal/mol} = -72 \text{ kJ/mol}$$

The properties for No. 2 diesel fuel represent the 10 percent maximum aromatics formulation that is available in California. No. 1 diesel fuel, kerosene, and Jet A are essentially the same fuel and are available across the country. No. 1 diesel is a lighter fuel and has a higher H/C ratio. LPG has a slightly different composition than pure propane. The formulation shown here represents LPG derived from oil refineries. LPG contains a few percent propylene and butane. LPG is stored in pressure vessels with a storage pressure of 190 psi. Natural gas contains about one percent CO_2 and nitrogen with traces of other hydrocarbons. The inert components reduce its heating value and raise its molecular weight. Methanol, ethanol, and hydrogen are generally distributed as pure compounds. The alcohol fuels may contain about 500 ppm water which does not have a significant impact on the properties shown in Table 3-2.

The properties for liquid fuels are shown for the fuels in their liquid state. If the fuels are vaporized prior to injection into a combustor, the available energy increases by the latent heat of vaporization.

The LPG specification for vehicles (HD-5) limits propylene content to 5 percent. The composition in Table 3-2 is based on measurements of LPG samples (Unnasch 1996).

Non hydrocarbon fuels are also potential feedstocks for fuel cells. Ammonia is an good energy carrier for hydrogen. It can be dissociated at low temperatures to form nitrogen and hydrogen. However, the widespread distribution of ammonia seems unlikely.

3.2 STEAM REFORMING

Steam reforming involves the reaction of hydrocarbon fuels with steam to produce hydrogen in an endothermic process. Figure 3-1 shows the schematic of a steam reformer system for PEMFC vehicles. It consists of the following components:

- Steam reformer (SR)
- External burner to provide heat for the reformer
- Low temperature shift reactor (LTS)
- Gas cleanup device
- Peripheral equipment to ensure proper operation, such as pumps, compressors heat exchangers, fuel preparation devices, etc.

The technical evaluation of steam reformer and external burners is given in this section. The remaining system components are described in subsequent sections.

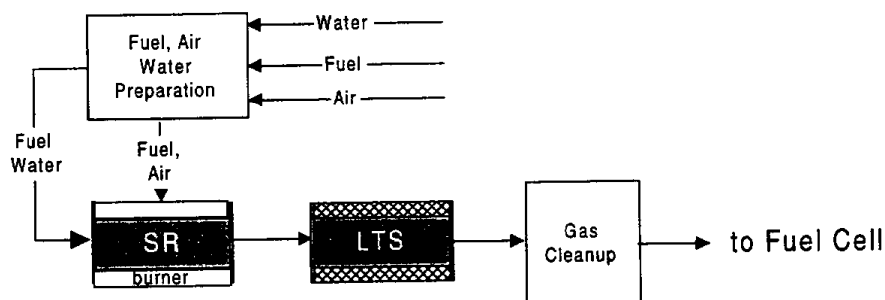


Figure 3-1. Schematic of a steam reforming system

Because the reaction is endothermic, additional heat must be supplied from an external heat source. A catalytic burner, which burns primary fuel as well as unused hydrogen from the fuel cell, is often used to provide external heat for the reactor. NO_x as well as unburned HC emissions from such a burner should be very low, because low combustion temperatures do not favor NO_x formation while lean operating conditions in the presence of a catalyst can result in minimum HC emissions. However, the burner must be carefully designed because low combustion

temperatures also tend to increase the potential for HC emissions. The fuel, which is available for the burner in fuel cell systems, changes from the primary fuel during start up conditions to primary fuel plus unreacted fuel-cell anode hydrogen during normal operation. Dynamic response for a steam reformer is limited by the need for heat transfer from the external heat source into the reformer. However, this constraint has not adversely affected the performance of SR systems on-board passenger vehicles.

Various hydrocarbon fuels can be converted to hydrogen in a steam reformer. The reforming reaction takes place at about 800°C with a nickel catalyst. These types of reformers are, therefore, less suitable for light-duty vehicles because the energy required for warm-up would have a significant impact on fuel economy. Heat losses and packaging constraints for SR systems make them more suitable for heavy-duty vehicles such as transit buses that operate over an extended period of time. Low temperature steam reformers for methanol do not have the same warm up constraints, and are therefore more suitable for passenger car operation. However, the low-temperature reformer/PEMFC system will likely require high purity methanol. The product gas from steam reforming has a considerable advantage over POX syngas because the SR gas contains over twice the hydrogen concentration and does not contain trace contaminants such as NO_x or ammonia.

Specific features of high and low temperature steam reforming systems are discussed below.

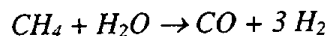
3.2.1 High Temperature Steam Reforming

The process for catalytic steam reforming was fully developed as early as 1930. Steam reforming of methane is one of the principal commercial processes for the production of hydrogen and synthesis gas (syngas). Natural gas, propane, and light hydrocarbons are typical feedstocks for industrial steam reformers. The following discussion covers the steam reforming of natural gas. The operating conditions and temperatures for other fuels are discussed at the end of this section.

Reforming natural gas involves desulfurization of the feedstock. The natural gas feedstock must be desulfurized prior to reaction over the steam reforming catalysts, because sulfur poisons the catalyst by deactivating the hydrogenation sites. Desulfurization typically consists of two steps. First, the gas passes over a Co-Mo or a Ni-Mo catalyst fixed bed at 290 - 400°C in the presence of hydrogen to convert all sulfur compounds to H₂S (Kirk and Othmer 1984, Hydrocarbon Processing, Haldor Topsøe, April 1984). Second, the hydrogen sulfide is adsorbed by a ZnO catalyst at 340 - 370°C, reducing the sulfur content to 0.5 ppm (Kirk-Othmer, Vol 12). Ambient temperature, adsorption-only methods are also available for sulfur reduction in natural gas feedstocks.

After desulfurization, the mixture of natural gas and steam is preheated and enters the catalyst bed of the reformer. The feed gas is preheated with the reformer product gas and burner exhaust gas. A burner provides heat for the reforming reaction. The burner gas is in contact with the tubes or vessel walls that hold the reforming catalyst material.

Steam reforming of methane to form syngas for methanol production proceeds via the following highly endothermic reaction:



$$\Delta H_{298} = 206.2 \text{ kJ/mol}$$

Steam reforming of methane for industrial hydrogen production uses a higher steam to CH_4 ratio (Kirk and Othmer 1984) than the 1:1 value for methanol syngas. The additional steam results in a higher hydrogen yield from the reformer because much of the CO can be converted to CO_2 . The steam reforming reaction produces a net increase in molar volume. As indicated above, one mole of CH_4 and H_2O produce 4 moles of product gas. Therefore, lower reaction pressures favor the formation of hydrogen and the equilibrium conversion decreases with increasing reaction pressures (Uemiya et al. 1991). Increasing the reformer temperature also favors the formation of hydrogen. The chemical equilibrium products of methane steam reforming are shown in Figure 3-2.

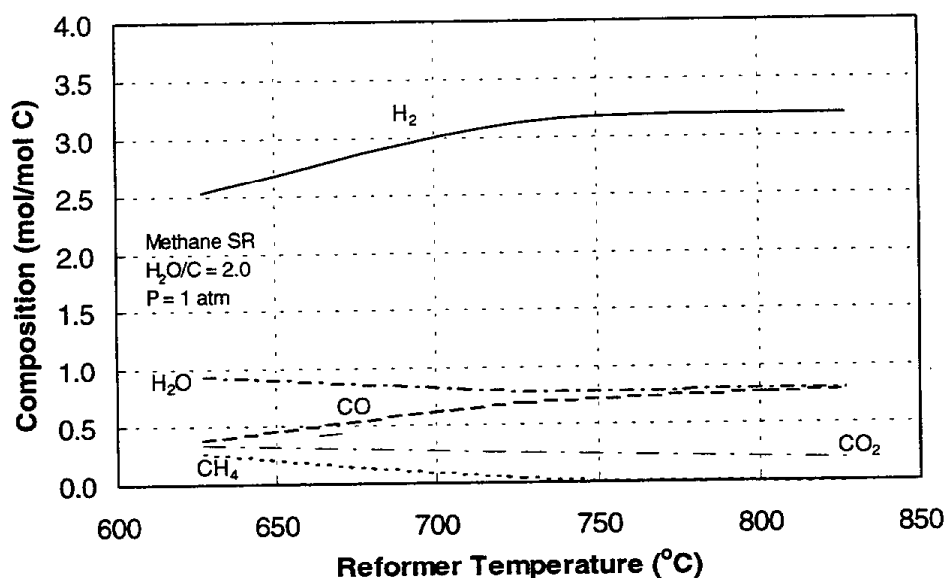


Figure 3-2. Methane steam reforming equilibrium composition ($\text{H}_2\text{O}/\text{C}=2.0$, 1 atm)

The methane steam reforming reaction typically occurs in the presence of catalysts. One study (Zhang and Baerns 1991) found that in the absence of a catalyst the steam reforming reaction of hydrocarbons such as methane, ethane, and ethylene, does not occur to a significant extent at temperatures below 800°C . These researchers found that a CaO-CeO_2 catalyst promoted the reaction to a significant extent at 800°C . Agnelli et al. (1987) found that the kinetics of the methane steam reforming reaction are first order with respect to methane partial pressure. Other studies have concurred with these findings (Al-Ubaid and Wolf 1987). In hydrogen production operations, nickel-based catalysts are typically used.

The product gas from the reformer further reacts in the water-gas shift reaction, which is slightly exothermic:



The water-gas shift reaction occurs within the reformer catalyst; however, lower CO levels can be achieved by operating a low temperature shift reactor (LTS). The water-gas shift reaction is used in industrial processes to remove excess CO, resulting in higher conversion to H₂. This reaction typically operates around 400°C in the presence of Fe-Cr or Cu-Zn-Cr catalysts (Kirk and Othmer 1984).

As Figure 3-2 indicates, a steam reformer operating on natural gas potentially can convert almost all of the methane into CO₂ and H₂.

Table 3-3 shows the theoretical maximum hydrogen yield for steam reforming of different fuels. If all of the fuel were converted to CO₂ and hydrogen, each mole of carbon would produce two moles of H₂, each mole of hydrogen would produce one-half mole H₂, and each mole of oxygen would subtract one mole of H₂. Therefore, natural gas and propane have the highest hydrogen production potential. The temperature requirements of steam reforming are similar for hydrocarbon fuels.

Table 3-3. Theoretical hydrogen yield from steam reforming of various fuels

Fuel	Formula	H/C	SR Product H ₂ (mol/mol C)	SR Product H ₂ mole fraction ^a (%)
Gasoline	C _{6.55} H _{13.26} (l)	2.024	3.01	75.1
RFG	C _{6.69} H _{13.65} O _{0.121} (l)	2.041	3.00	75.0
Diesel No. 2	C _{12.4} H _{21.15} (l)	1.706	2.85	74.0
Diesel No. 1	C _{11.1} H _{20.27} (l)	1.826	2.91	74.4
Iso-octane	C ₈ H ₁₈ (l)	2.25	3.13	75.8
LPG	C ₃ H _{7.88} (l)	2.626	3.31	76.8
Propane	C ₃ H ₈ (l)	2.667	3.33	76.9
Natural Gas	CH _{3.85} O _{0.019} N _{0.031} (g)	3.85	3.91	79.6
Methane	CH ₄ (g)	4	4.00	80.0
Methanol	CH ₃ OH (l)	4	3.00	75.0
Ethanol	C ₂ H ₅ OH (l)	3	3.00	75.0

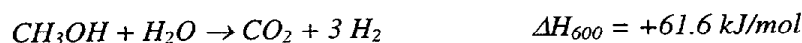
^a Dry Basis. Theoretical yield is a mixture of H₂ and CO₂.

3.2.2 Low Temperature Methanol Steam Reforming

Steam reforming of methanol can also occur at lower temperatures with a copper/zinc catalyst. Catalysts for methanol reforming selectively allow for the dissociation into CO and hydrogen from methanol. High temperature reforming involves methane as an intermediary species and

methane reforming must take place at high temperatures as indicated in Figure 3-2. Low temperature methanol reforming occurs at temperatures between 230 and 300°C.

One mole of methanol reacts with one mole of water vapor to produce three moles of hydrogen with the complete reaction:



The two steps in the reaction are the endothermic reforming of methanol and the exothermic water-gas-shift reaction, as follows:



The water-gas-shift reaction at temperatures of interest results in traces of CO in the reactor effluent. A shift catalyst bed may be incorporated into the end of the reformer catalyst to minimize CO levels. The low temperature shift reaction occurs at the same temperature as the reforming reaction. In order to obtain low CO-levels as well as high methanol conversion and reactor volume, Colsman indicates that the optimum water/methanol ratio is 1.3, leaving 0.3 moles of unreacted water per mole of methanol in the reformer effluent. Figure 3-3 shows the effect of water/methanol ratio on methanol conversion. The methanol and CO content in the reformer effluent continue to drop off as more water is added which results in further hydrogen production. Other factors affected by the water/methanol ratio are the heat required for water vaporization and fuel cell system integration issues such as water recovery. These factors also need to be considered when selecting an operating point.

Figure 3-4 shows the effect of pressure on methanol conversion in a low temperature steam reformer. The methanol content of the reformer effluent drops with a drop in pressure while CO and other components are unaffected. The synthesis of methanol, which is the opposite of the reforming reaction, occurs under similar conditions except at high pressures¹.

¹The production or synthesis of methanol occurs at the same temperature and high pressure (30 atm) as low temperature methanol steam reforming with a similar catalyst material. The formation of methanol is not thermodynamically favored and only 15 percent of the syngas is converted to methanol in a single pass over the catalyst. By reducing the pressure of the catalytic process, equilibrium favors very low methanol concentrations with the balance of gas being a mixture of H₂, H₂O, CO, and CO₂.

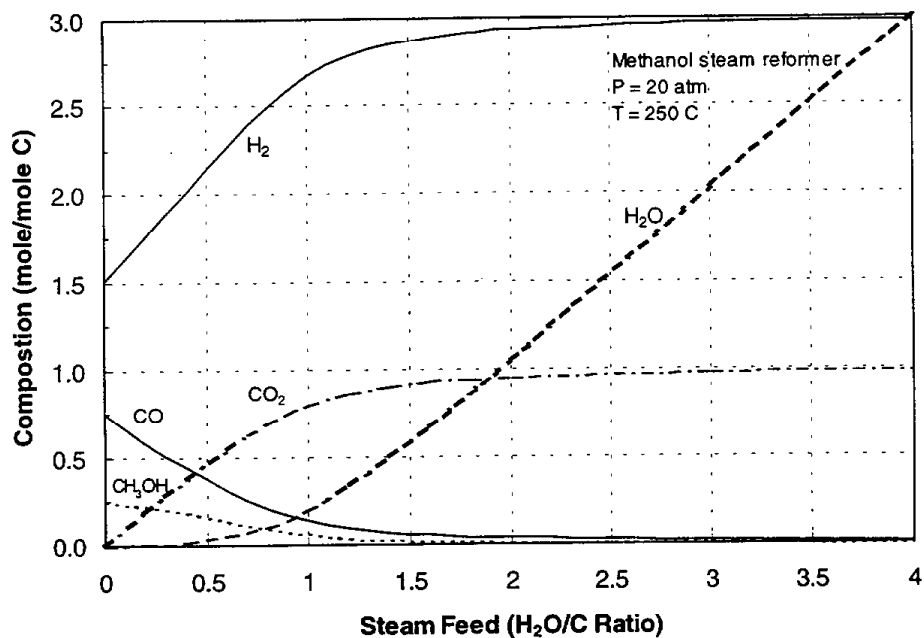


Figure 3-3. Effect of steam feed methanol steam reforming equilibrium composition

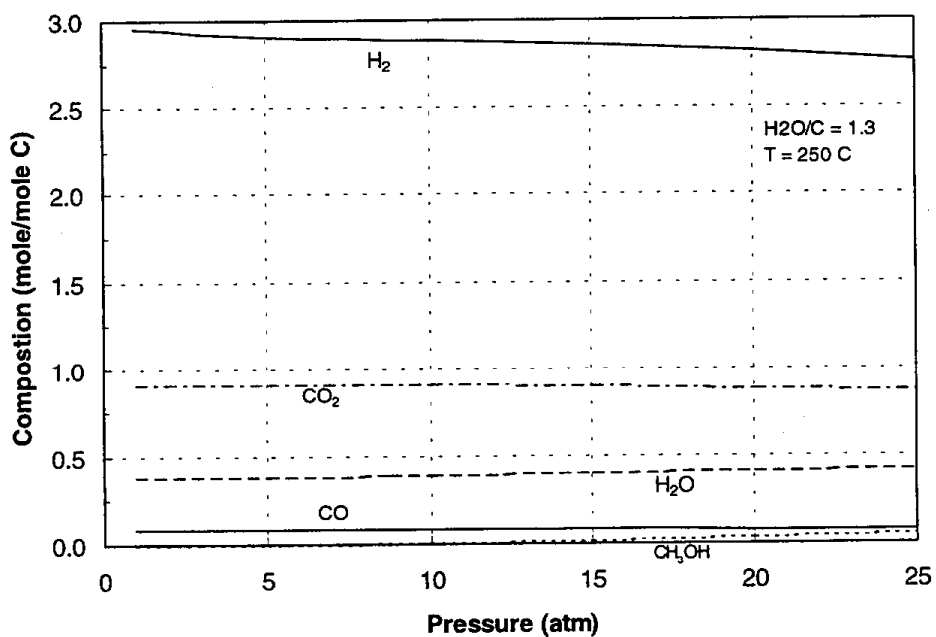


Figure 3-4. Effect of pressure on methanol steam reforming equilibrium composition, H₂O/C=1.3

The catalyst for reforming methanol does not convert impurities such as high alcohols or hydrocarbons to a significant extent. Therefore, if fuel grade methanol formulations are used in fuel cell powered vehicles, the unreacted impurities may reduce the fuel cell efficiency. Some fuel specifications, including ARB's specification for M100 allows 2 percent higher alcohols and hydrocarbons as well as 1000 ppm water. Table 3-4 shows the pertinent specifications for M100 fuel that would result in impurities in the effluent of a low temperature steam reformer. A separate specification may need to be considered for some types of fuel cell vehicles with methanol steam reformers. However, a special fuel formulation for this technology would complicate the development of a large scale infrastructure for methanol.

Table 3-4. California specifications for M100 fuel

Parameter	Specification
Methanol	98 % min.
Higher alcohols	2 % max.
Hydrocarbons	2 percent max.
Water Acidity	1000 ppm max.

The Forschungszentrum (Research Center) Jülich / Germany (FZJ), Los Alamos National Laboratory (LANL), General Motors/Delphi, and Argonne National Laboratory (ANL) have performed research on methanol steam reformers to produce hydrogen for fuel cell powered vehicles. Reforming methanol provides a syngas of sufficient quality for direct feed to a PAFC which is less sensitive to impurities like CO than the PEMFC.

Several vehicle manufacturers are using low temperature methanol steam reformers in their system design. GM/Delphi is building a low temperature reformer for the GM fuel cell powered car. The Fuji methanol SR system is based on a low temperature steam reformer. Ballard is supplying the fuel cell for Phase IV of the Georgetown University bus program. This system will consist of a PEMFC with a low temperature steam reformer. Methanol steam reformer systems have also been under development in Europe. In order to take advantage of the low temperature operation of the SR system, a burner must be integrated with the reformer. A catalytic burner shown in Figure 3-5 is particularly suitable for this application. The FZJ has completed extensive development on a catalytic combustion of methanol and anode tail gases (Colsman). Halder Topsøe has designed an integrated reformer system for vehicle applications that packages the burner with the reformer and shift reactor and provides preheating of the reformer feed. This design is shown in Figure 3-6.

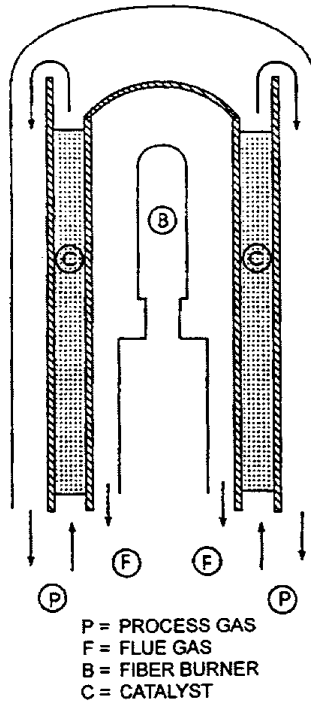


Figure 3-5. Ring burner configuration for a low temperature methanol steam reformer

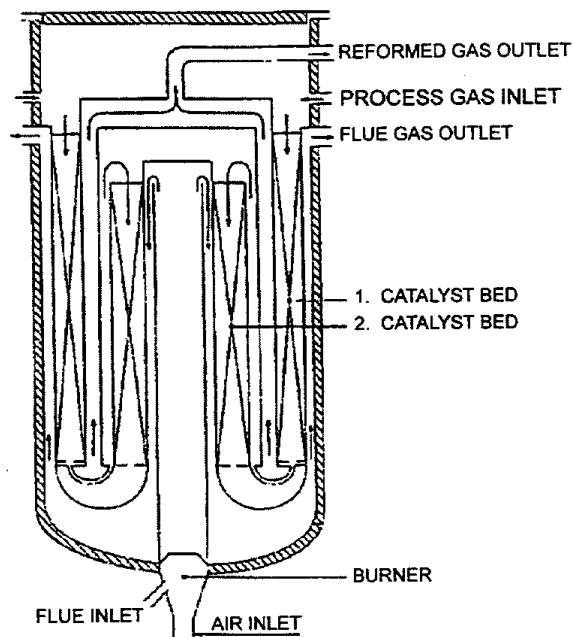


Figure 3-6. Halder Topsøe Integrated low temperature methanol steam reformer

3.3 PARTIAL OXIDATION (POX)

POX reforming involves the substoichiometric burning of fuel with oxygen or air. An important advantage of POX over low temperature methanol steam reforming is that a POX system can operate on any hydrocarbon feedstock from natural gas to crude oil.

A POX system schematic is shown in Figure 3-7.

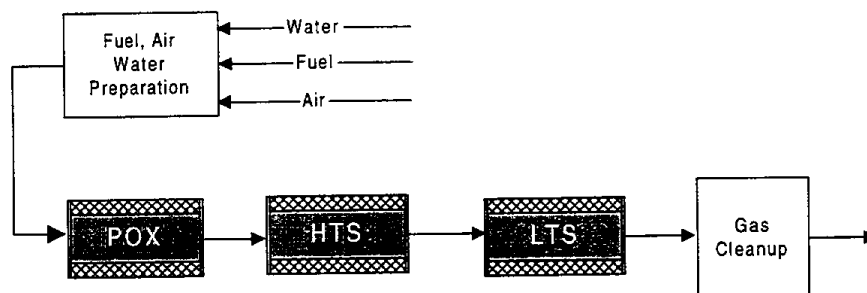


Figure 3-7. Schematic of a POX system

A POX system consists of the following components:

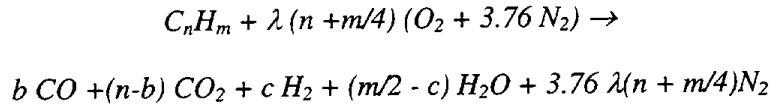
- Partial oxidation reactor (POX)
- High temperature shift reactor (HTS)
- Low temperature shift reactor (LTS)
- Gas cleanup device
- Peripheral equipment to ensure proper operation, such as pumps, compressors, heat exchangers, fuel preparation devices, etc.

The POX, HTS, and LTS are described below. The gas cleanup and peripheral equipment are described in Sections 3.4 and 3.5, respectively.

3.3.1 Partial Oxidation (POX) Reactions

The hydrocarbon feedstock, water and air are fed into a reaction-chamber after vaporization, preheating, and pressurization. The required heat for the reaction is supplied in-situ by oxidizing a fraction of the feedstock. The extent of the oxidation reaction is regulated by the mixture stoichiometry. Large scale industrial POX processes typically use pure oxygen, so that the later purification of the hydrogen is less costly, but air is the only the feasible oxidant for vehicle applications and small scale stationary industrial systems.

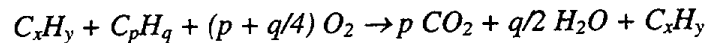
The preheated and vaporized reactants are injected through a specially designed burner into a combustion vessel, where POX occurs at 1000 to 1220°C. The oxygen content represents a rich or substoichiometric mixture, so all of the oxygen is consumed in the reaction. The overall reaction is represented by:



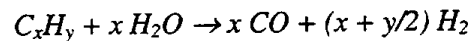
where the stoichiometric ratio, λ , represents the ratio of available oxygen to oxygen required for a stoichiometric mixture. The amount of hydrogen produced represented by c , depends on equilibrium, reaction kinetics, and other reactor design considerations. Nitrogen, as the main component of air, is inert to the catalyst of PEMFCs. Nitrogen does act as a diluent to the anode feed; however, the effect on fuel cell voltage performance is minimal.

This overall reaction can be divided into three steps:

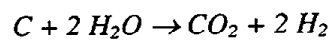
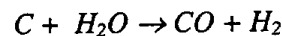
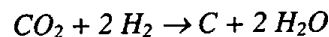
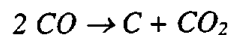
- Step 1: Heating and cracking phase. Preheated hydrocarbons leaving the atomizer intimately contact with the steam-preheated air mixture. The preheated hydrocarbons are heated further by back radiation from the flame front and the reactor walls. Some cracking to methane, carbon and hydrocarbon radicals can occur during this initial phase.
- Step 2: Reaction phase. Hydrocarbons react with oxygen according to highly exothermic combustion reaction. Practically all the available oxygen is consumed during this phase. The reaction is:



The remaining unoxidized hydrocarbons, $C_x H_y$, react endothermically with steam and the combustion products from the primary reaction. The main endothermic reaction is reforming of hydrocarbons by water vapor:

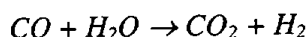


Competing reactions include the formation of carbon and reaction of carbon with steam:



These reactions show how steam addition suppresses carbon formation. Soot formation is also suppressed at higher temperatures and favored at lower temperatures. Therefore, cool reactor walls can initiate soot formation. Subsequent rapid quenching of the gas mixture lowers the temperature to a point where soot formation is eliminated.

Step 3: Soaking phase. The final phase takes place in the rest of the reactor where the gas mixture is at high temperatures. Specifically, the exothermic water gas shift reaction takes place:



These reactions result in a thermal energy events which affect the reactor temperature. The extent to which the reaction reaches equilibrium depends upon the design of the reactor and the reactor temperature.

3.3.2 Theoretical POX Reactions for Hydrocarbons

As an example of the theoretical conversion of a hydrocarbon fuel and air, Figure 3-8 shows the equilibrium chemistry products for octane in a POX reactor which is fed with fuel and air at ambient temperature. The gas compositions are shown on a mole per mole of carbon in the feedstock basis. At rich stoichiometries, ($\lambda < 0.45$) solid carbon is formed. Solid carbon disappears as more oxygen is added. The presence of solid carbon can result in fouling of a non-catalytic POX reactor. Hydrogen production, however, is greatest at low stoichiometries. The best figure of merit for a fuel cell reformer may be hydrogen plus CO as the CO can be converted to hydrogen in a shift reactor. The sum of hydrogen and CO reach a peak around $\lambda = 0.45$; however, this region still forms solid carbon. As the stoichiometry is increased, carbon formation is eliminated, the reactor temperature increases, and total hydrogen and carbon production decrease as more CO₂ and water vapor are produced. As discussed in the following section, increasing the inlet temperature and adding steam to the reactor improves its performance substantially.

3.3.3 Real World POX Reactor Issues

The important variables in real world POX reformer operation are:

- Fuel air stoichiometry
- Operating temperature of the POX vessel
- Feed temperature (residence time at reaction temperature)
- Steam content of feedstream
- Fuel type

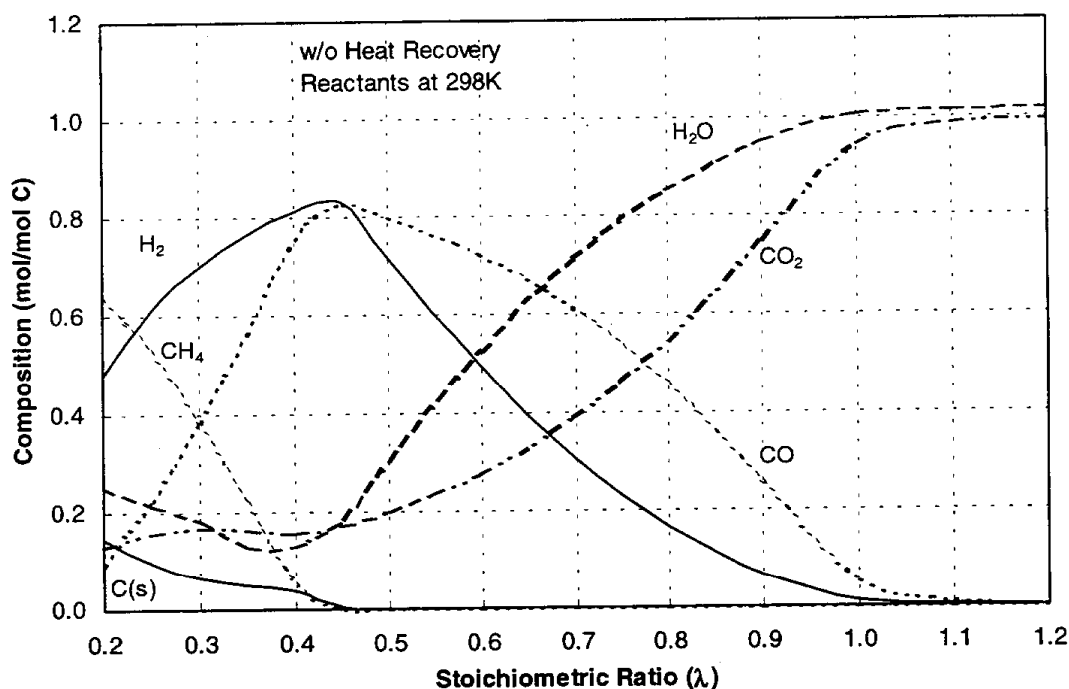


Figure 3-8. Partial oxidation of octane equilibrium composition, $H_2O/C = 0$, no preheat of air and fuel

Real world POX systems do not perform as well as those predicted by equilibrium. The principle shortcomings of real world systems are the formation of solid carbon and higher methane compositions which reduce hydrogen yield. Solid carbon also plugs the POX reactor and downstream catalysts. In general, hydrocarbons are cracked to form methane fairly rapidly and unreacted hydrocarbons do not represent a significant fraction of a real POX reactor effluent. Adding steam to the reactor feed can suppress carbon formation. The effect of solid carbon is even more troublesome for catalytic autothermal reactors where the catalyst can be coated and deactivated.

Higher reactor temperatures favor a more complete reaction to equilibrium because the rates of reaction are higher at elevated temperatures. Two methods are possible for increasing the reactor temperature. Either operate the reactor at a leaner stoichiometry or preheat the air and fuel to provide a higher energy input into the reactor. Thorough mixing of air and fuel can also be very important in the reactor design. If stratification of fuel occurs, it may travel through a portion of the reactor without cracking. A delay in cracking the fuel will result in less time in the reactor, reducing the time available for other reactions, and, subsequently, a less complete approach to equilibrium.

Raising the feedstock temperature is favorable in terms of efficiency and fuel conversion. Figure 3-9 illustrates the effect of heat recovery on the POX system. The equilibrium gas compositions and reaction temperatures depend on the inlet air and fuel temperatures. For the curves with heat recovery, the air and fuel temperatures are based on recovering heat available from the POX and subsequent reactor steps. Comparing the results “with-heat-recovery” shows an increased temperature as well as reduced carbon formation at richer stoichiometries. Preheating the air and fuel increases the peak $H_2 + CO$ from 1.7 to 1.85 and reduces the minimum stoichiometry for carbon formation.

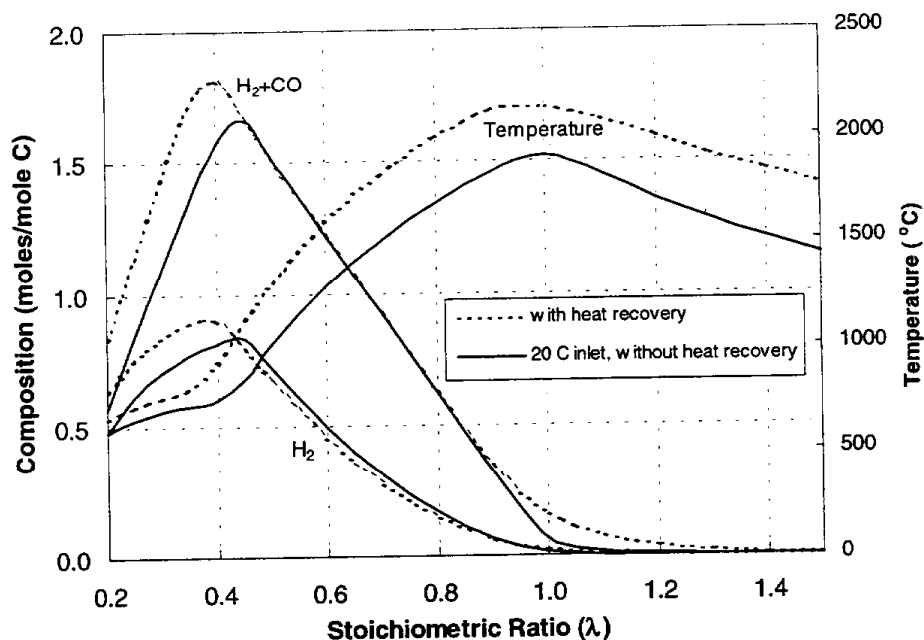


Figure 3-9. Effect of preheating input gases on POX of n-octane, $H_2O/C=0$

Such an approach requires an integrated heat recovery design to avoid the use of exotic materials, such as high temperature alloys, in the reactor.

Adding steam to the POX inlet suppresses carbon formation and increases the hydrogen produced from the reactor. Adding steam also affects heat transfer within a POX system as water must be converted to steam and the steam preheated. Figure 3-10 examines the effect of steam addition on a POX reactor with n-octane. With an H_2O/C ratio of 0.5, carbon formation is suppressed at temperatures above 750°C while solid carbon would still form at 900°C with an H_2O/C ratio of 0.1. Total hydrogen plus CO is higher with more steam added for a given temperature. However, adding steam reduces the temperature of the POX reaction. Therefore, the system design must include sufficient heat transfer to preheat steam and air to maintain a sufficiently high product gas temperature. The temperature of the reactor output also decreases which reduces the net hydrogen and CO production.

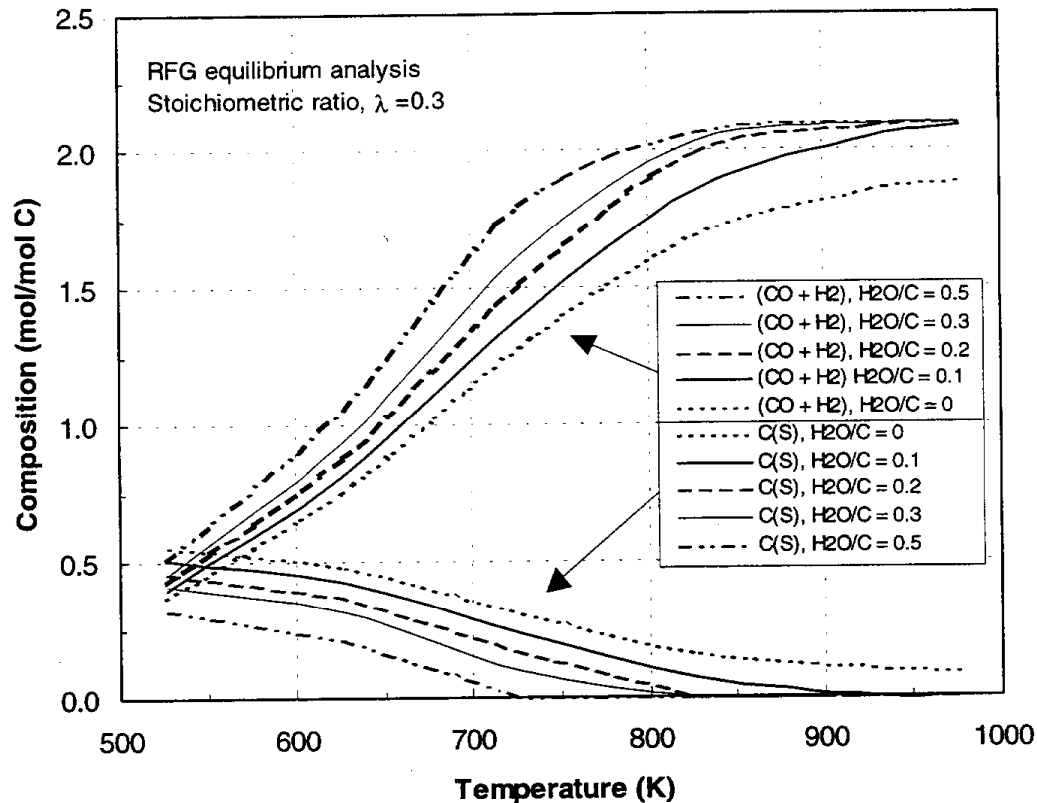


Figure 3-10. n-Octane POX equilibrium carbon formation and hydrogen yield with various stoichiometries and H_2O/C

Figure 3-11 shows the effect of steam addition over a range of stoichiometries. The sum of CO and hydrogen reflects the potential hydrogen yield from the reaction with the balance of CO converted to CO_2 in the shift reactor. The addition of steam is beneficial because it suppresses solid carbon formation and improves fuel atomization. Steam addition also plays a role in heat recovery and cooling of the POX reactor. Therefore, steam/carbon ratios of 0.25 to 0.5 would be optimal for a POX system.

Figure 3-12 shows the predicted reaction temperatures for n-octane with heat recovery that is used to increase the inlet temperature of the air, fuel, and steam. Depending upon stoichiometry, air is preheated to approximately 700°C. At rich stoichiometries, gas flows are lower which increases heat transfer rates so a slightly higher air preheat is possible. As the stoichiometry increases, the flow of air and POX temperature both increase which tends to maintain an preheat temperature of approximately 700°C. Preheating the input air, steam, and fuel increases the POX output temperature. Higher POX operating temperatures favor a more complete reaction and lower methane in the product gas. Material limitations make operation at above 1500°C undesirable.

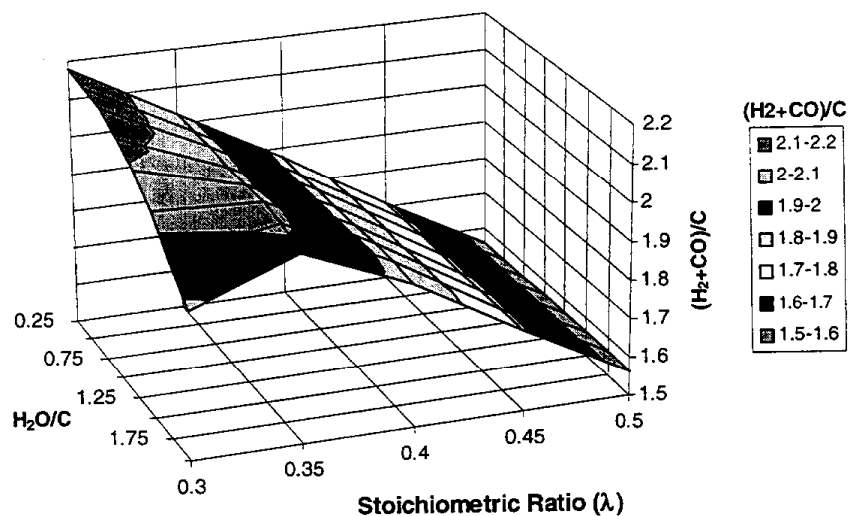


Figure 3-11. n-Octane partial oxidation equilibrium composition with various stoichiometries and H_2O/C

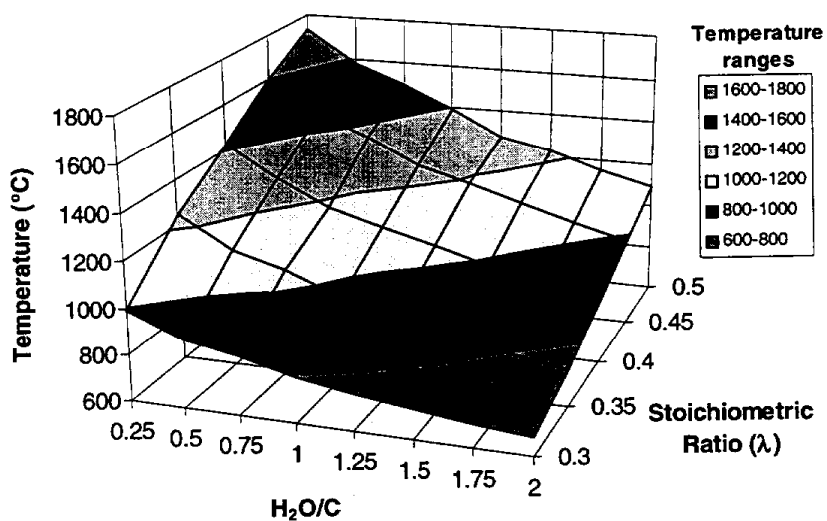


Figure 3-12. n-Octane partial oxidation adiabatic flame temperature with various stoichiometries and H_2O/C

Figure 3-13 shows the partial oxidation temperature with preheated air and fuel for various fuels. Energy for preheating is extracted from the POX unit.

Figures 3-14 through 3-19 show the equilibrium compositions for POX effluent for the fuels considered in this study with a steam to carbon ratio of 0.5. The predicted temperature is based on a model of a POX reactor system that includes heat loss from the reactors and heat recovery for air, steam, and fuel. The heat recovery results in an increased reactor temperature and improved real world performance. A modest increase in equilibrium hydrogen and CO are also achieved. A peak in hydrogen production occurs for hydrocarbon fuels at approximately $\lambda=0.33$. The peak is at a lower stoichiometry for methanol and ethanol. Natural gas results in the highest rate of hydrogen production. These parameters are inputs into the model of fuel cell powered vehicle efficiency.

For low methane production and no carbon conversion, POX reactors should operate as follows:

- High stoichiometry with a reduced hydrogen yield and high reactor temperatures which require insulation or cooling
- High steam/carbon ratios which reduce carbon formation but may result in incomplete reaction (high methane content and low conversion efficiency)

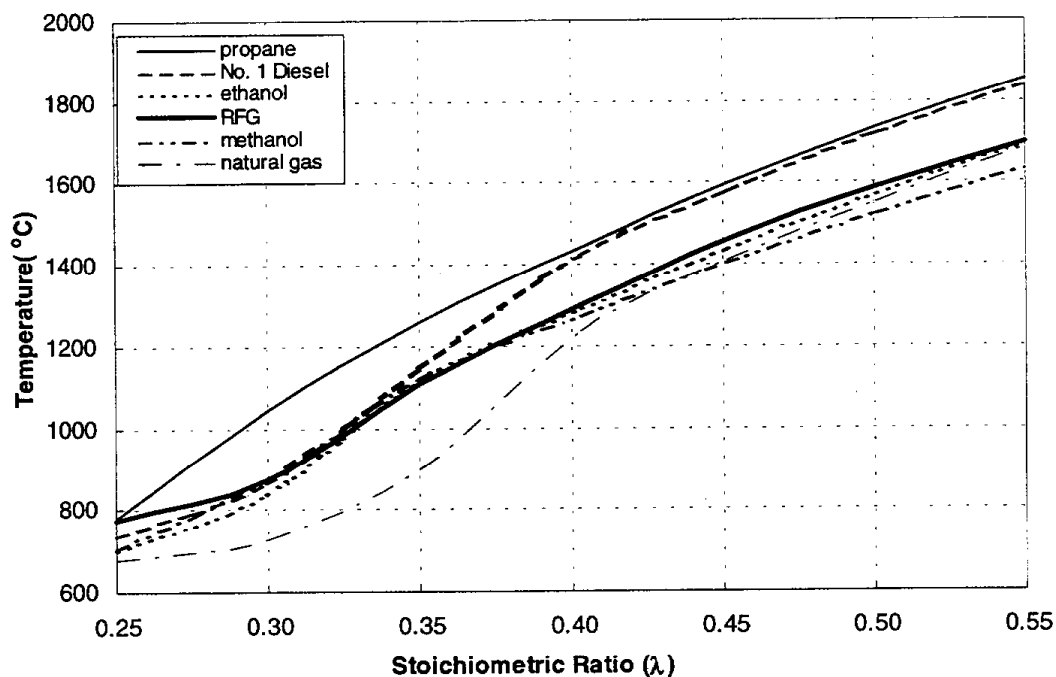


Figure 3-13. Operating temperature of the partial oxidation reactor for various fuels with inlet air and fuel preheating

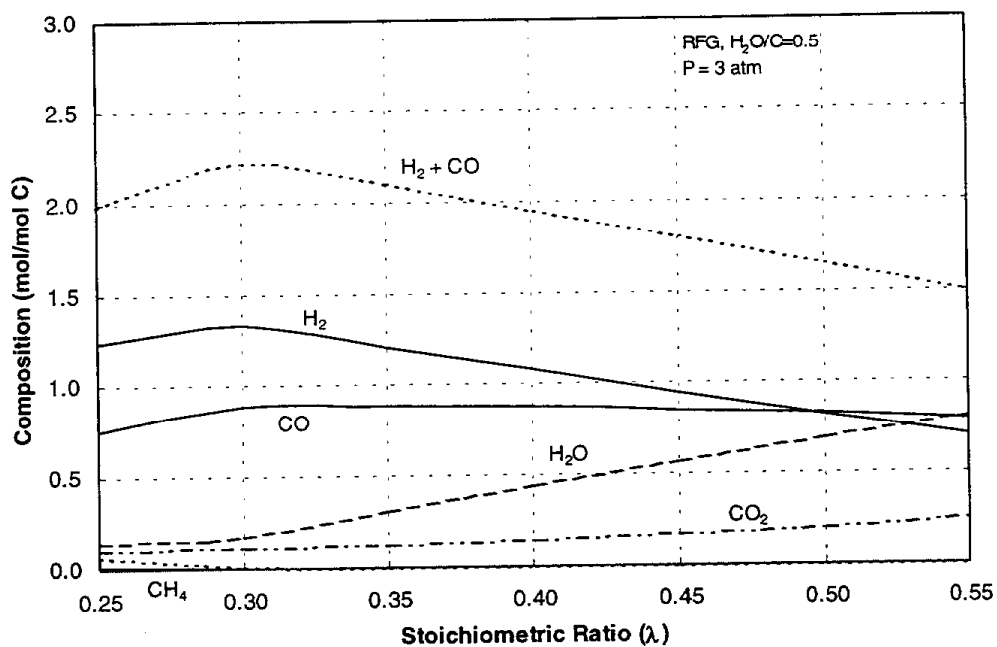


Figure 3-14. RFG partial oxidation equilibrium composition, $H_2O/C = 0.5$

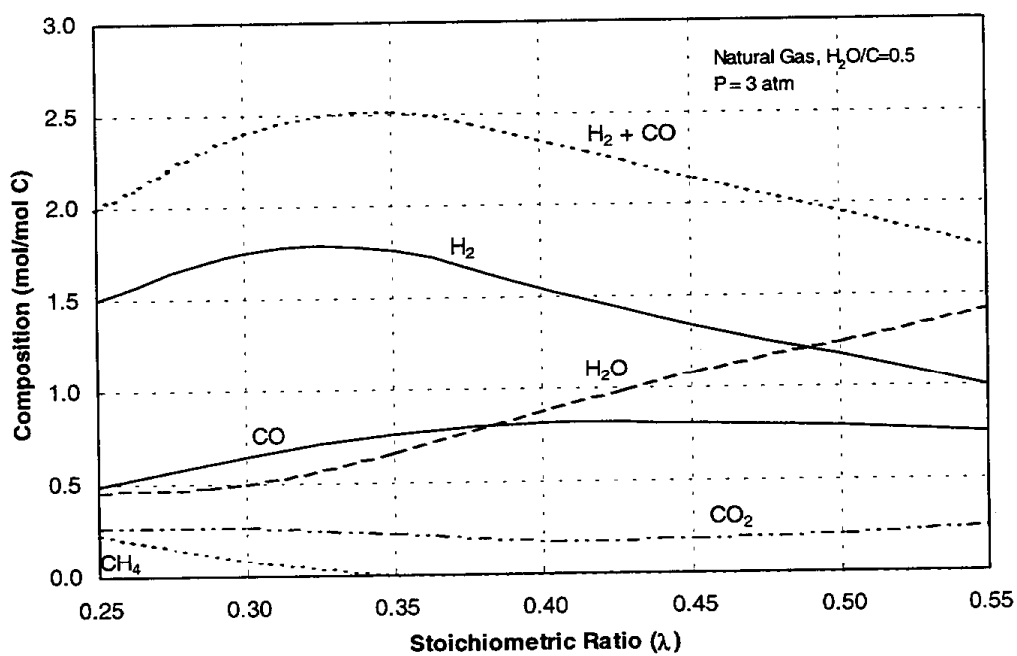


Figure 3-15. Natural gas partial oxidation equilibrium composition, $H_2O/C = 0.5$

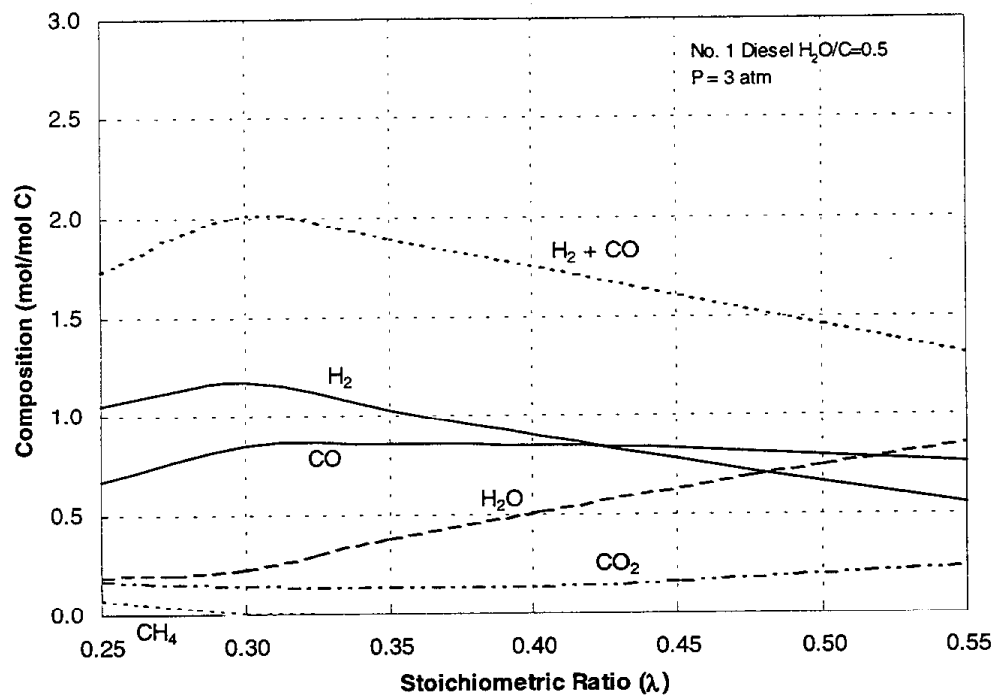


Figure 3-16. No. 1 Diesel partial oxidation equilibrium composition, $H_2O/C = 0.5$

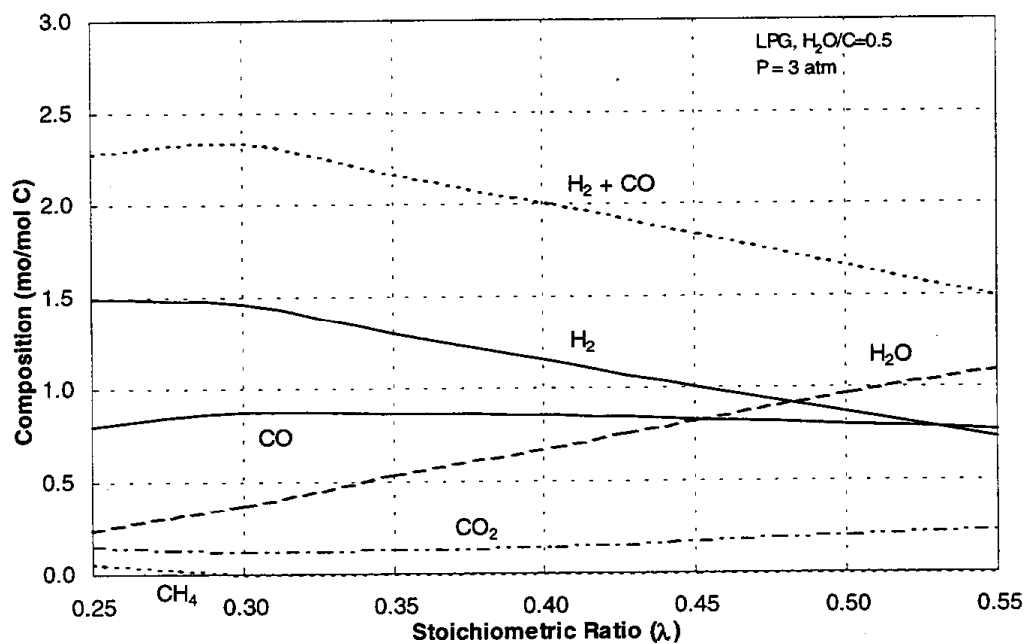


Figure 3-17. LPG partial oxidation equilibrium composition, $H_2O/C = 0.5$

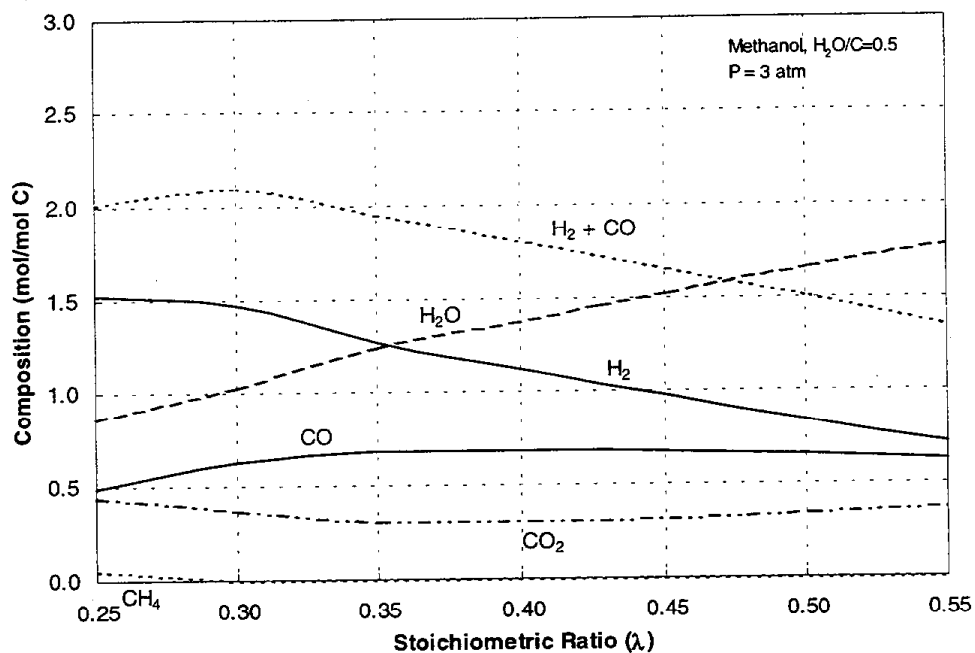


Figure 3-18. Methanol partial oxidation equilibrium composition, $H_2O/C = 0.5$

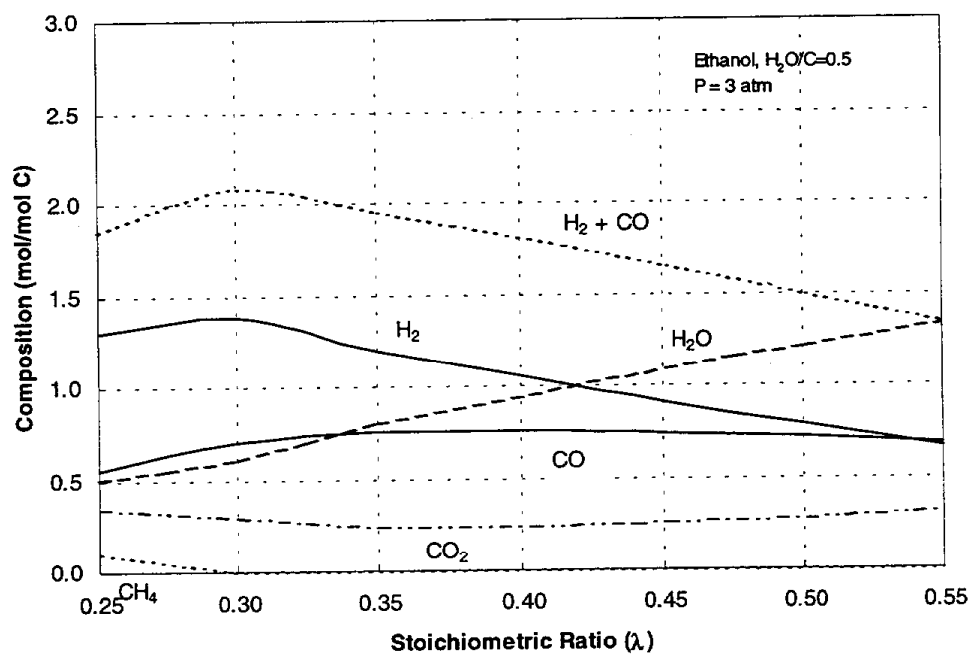


Figure 3-19. Ethanol partial oxidation equilibrium composition, $H_2O/C = 0.5$

- Low stoichiometry with very high preheat of air and steam to raise reactor temperature.

Table 3-5 shows the efficiencies of various fuels in a POX system. The efficiency is calculated from the product $\text{CO} + \text{H}_2$ and the inlet fuel lower heating value LHV on a cold gas basis. Less steam is also required for methanol. The efficiency results depend to a large degree upon the integrated heat recovery in the POX fuel processor system. Sufficient heat must be recovered from the POX reactor to preheat air and steam. Air preheat temperatures must not however be too high or materials in the POX reactor will experience a reduced lifetime.

Table 3-5. Theoretical hydrogen yield from partial oxidation with steam addition for various fuels

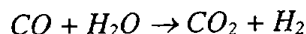
Fuel	Optimum Stoichiometry (λ)	Peak $\text{CO} + \text{H}_2$ (mol/mol C)	Theoretical POX efficiency ($\text{H}_2 + \text{CO}$)/fuel LHV
RFG	0.31	2.15	87%
Diesel No. 1	0.32	2.05	86%
LPG	0.32	2.3	88%
Natural Gas	0.34	2.5	88%
Methanol	0.27	2.1	87%
Ethanol	0.28	2.1	87%

^a Theoretical yield is a mixture of H_2 and CO . Yield depends on integrated air and steam preheat assumptions for each fuel. Efficiency represents cold gas heating value/liquid fuel heating value.

Partial oxidation is limited by the design and reaction kinetics in the reactor. If the reaction temperatures are too low or poor mixing occurs, then unreacted fuel, or by product methane will be present in the POX effluent with an adverse impact on conversion efficiency. Increasing the stoichiometry of the fuel/air mixture increases temperatures and improves the conversion of hydrocarbons towards equilibrium; however, the potential hydrogen yield is reduced. Designing the POX with integrated heat transfer allows for increased POX temperatures while operating at lower stoichiometric ratios (less air input). The heat transfer for preheating the air also cools the materials and allows less expensive components to be used in the system. ADL has performed extensive evaluations with ethanol on their reformer system. Under adverse operating conditions, high levels of methane can be produced (1 percent). However, when the operating temperatures and catalyst space velocity are carefully managed, low methane levels are achievable (Mitchell).

3.3.4 High Temperature Shift

The effluent from reformers contains CO which can be reacted with steam to produce additional hydrogen through the water-gas shift reaction:



This reaction is slightly exothermic. Two reactors are typically used for the shift reaction to take advantage of higher reaction rates at higher temperatures and lower CO concentrations at lower temperatures. At temperatures of about 500°C, the high temperature shift (HTS) is accelerated with an iron oxide catalyst (Twigg). Liquid water is injected into the POX effluent in order to achieve the temperature drop required for the HTS inlet. Higher H₂O/CO ratios favor a higher hydrogen production. A second shift reactor operating at 150 to 250°C can reduce CO levels to about 1 percent.

The HTS can be operated over a range of temperatures. At higher temperatures, the conversion of CO to CO₂ is lower, but the reaction rate is higher, and the catalyst will be less prone to aging. At temperatures as low as 300°C, the CO content can be as low as 2 to 4 percent; however, this performance can be affected by aging and requires a larger catalyst bed than an HTS operating at higher temperatures.

The effect of temperature (T) on the CO equilibrium is given by:

$$K_p(T) = K_{co} e^{(-E/RT)} = [CO_2][H_2]/[CO][H_2O]$$

This relationship is plotted in Figure 3-20.

3.3.5 Performance of an Integrated POX/HTS Fuel Processor

Hydrogen Burner Technology (HBT) of Long Beach, California, builds a partial oxidation system for industrial hydrogen production. Their Underoxidized Burner (UOB™) technology can be designed to work with any hydrocarbon fuel. HBT manufactures systems that operate on natural gas and propane for commercial use.

HBT has been developing a non-catalyzed reforming approach over the past 6 years and has experience with methanol reformers. This non-catalyzed reformer approach has many advantages including complete fuel flexibility and inter-changeability, tolerance to impurities, simple design and construction, low cost fabrication, rapid response and direct control. These features are required for a successful, high efficiency reformer that operates with or without catalyst and that uses ambient air as the oxidant source. HBT's test experience on various fuels include natural gas, diesel, gasoline, methane, and propane as well as various oxidants from air to 50% O₂.

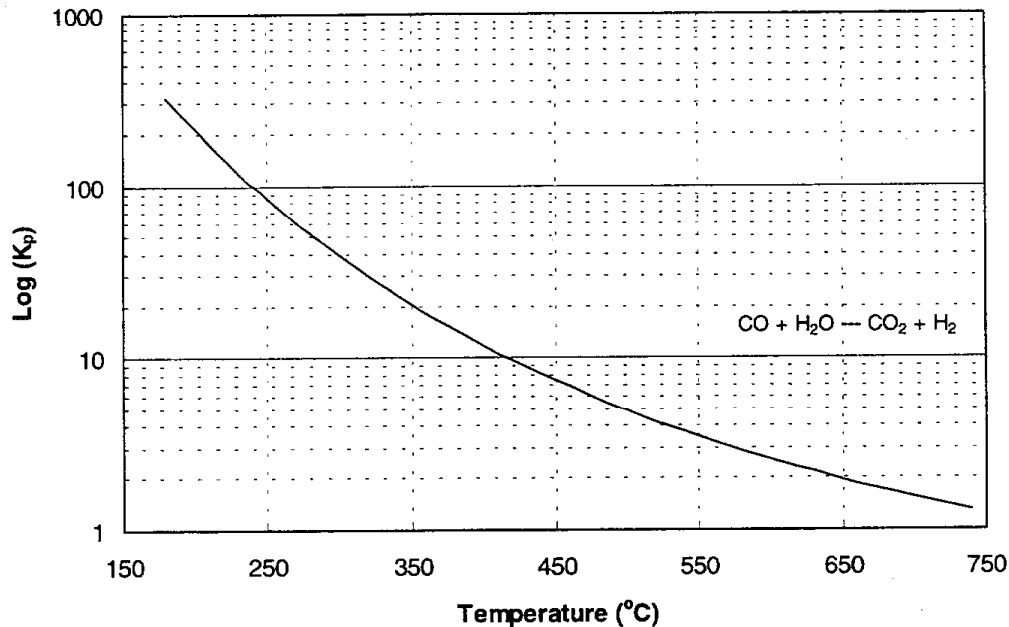


Figure 3-20. The water gas shift equilibrium favors lower CO concentrations at lower temperatures

The HBT system operates with a high fuel conversion and low methane content in the HTS exit gas. The methane concentration for an HBT industrial system operating on natural gas is below 0.05 percent. Figure 3-21 shows experimental data on the performance of the HBT UOB™ system operating on a variety of fuels with both air and oxygen feed. The data are very close to equilibrium levels over the range of stoichiometries tested. The industrial POX system does not incorporate steam addition to suppress carbon formation. Steam addition would also reduce the operating temperature of the system which is a trade off that needs to be considered for vehicle systems.

The industrial system operates at a leaner stoichiometry ($\lambda=0.45$) and higher pressure (20 atm) compared to the design conditions for vehicle systems ($\lambda=0.33$, 3 atm). HBT has also developed a system for vehicular applications and done work with diesel, gasoline, and methanol. A schematic of the system is shown in Figure 3-22. Air and fuel are preheated within the burner. Water is injected downstream of the burner to quench the POX reaction and provide steam for the shift reaction. The shift reactor is located downstream of the burner within the same vessel. A sulfur removal bed and CO removal catalysts would be situated downstream of the HTS catalyst.

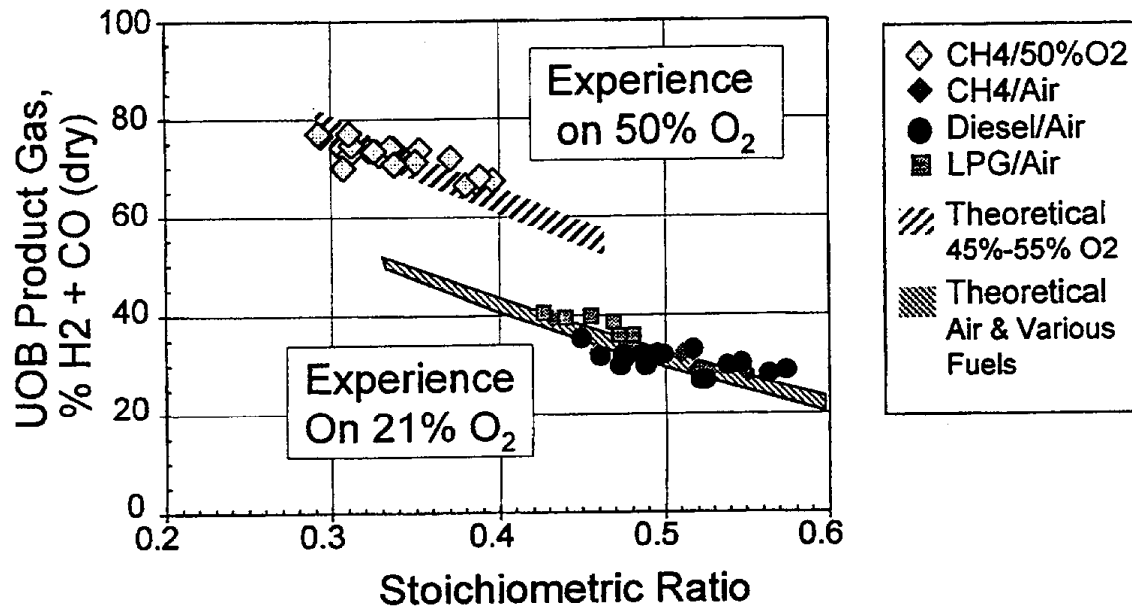


Figure 3-21. Hydrogen and CO yield from HBT UOB™ partial oxidation system

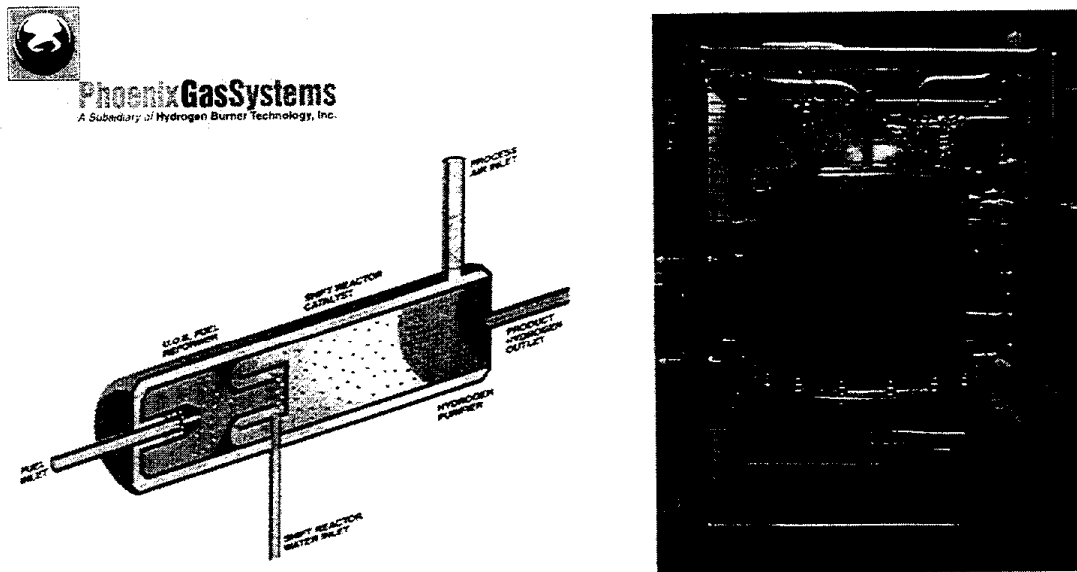


Figure 3-22. HBT UOB™ partial oxidation system for vehicle applications

3.3.6 Low Temperature Shift Reactor

A heat exchanger is required to cool the HTS-effluent to temperatures of about 200°C before it enters the low temperature shift reactor (LTS), where the second step of the water gas shift reaction takes place. Catalysts are commonly copper-based (Twigg). Copper remains active at temperatures below 200°C; however, copper is susceptible to sintering at temperatures above 250°C.

Figure 3-23 shows the calculated equilibrium CO concentrations and data for reformer effluent products. Reducing temperature and increasing feed stream concentrations reduce the CO output from the LTS. Differing gas composition products between steam reformers and POX systems account for most of the variation in CO concentrations in Figure 3-23. The effect of CO on fuel cell performance of fuel cells is typically represented on a ppm basis. However, if total moles of CO available to the electrocatalyst is the limiting parameter, then steam reformer feed with CO levels at twice the level of POX feed would have the same effect on PEMFC performance since the gas flow to the POX fed system is twice that of a steam reformer system.

The performance of an LTS reactor is affected by the following parameters:

- Catalyst size which is characterized by space velocity
- Condensing of water vapor at lower temperatures

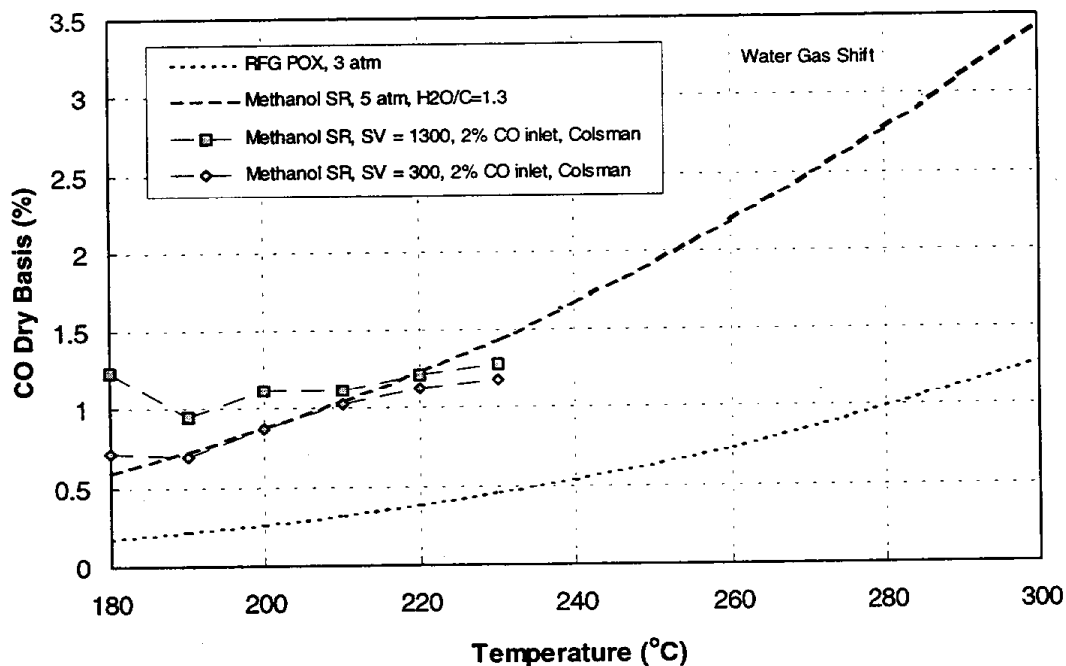


Figure 3-23. Low temperature shift data and equilibrium concentrations (Colsman)

- Heat release from the water gas shift reaction
- Low CO equilibrium at lower temperatures
- Higher reaction rates at higher temperatures

Current experimental data indicate that CO concentrations ranging from 0.5 to 1.0 percent are achievable from the LTS. Figure 3-23 includes experimental data on the operation of an LTS with feed gas from a methanol steam reformer containing 2 percent CO (Colsman). CO reduction improved with a reduction of catalyst space velocity. The space velocity is the ratio of catalyst feed (normal liters [NL] per minute) to the catalyst volume (liters [L]) with units of inverse hours (h^{-1}). The space velocity is inversely proportional to the residence time in the catalyst. Data from Colsman covered a space velocity range from 300 to 6500 h^{-1} . At high space velocities ($> 1000 \text{ h}^{-1}$), a minimum CO conversion was achieved in the temperature range from 210 to 220°C.

Reducing space velocity dominates the CO conversion at temperatures below 200°C with the catalyst performance being rate limited.

At space velocities below 600 h^{-1} , CO levels were reduced with a reduction in catalyst temperature. These data suggest a limit on the practical performance of an LTS as low space velocities correspond to catalyst volumes that may be too large for vehicle packaging. For a 60 kW fuel cell, with a hydrogen consumption of 40,000 NL/h and total gas flow of 60,000 NL/h from a methanol steam reformer, a space velocity of 1000 h^{-1} would correspond to a catalyst volume of 60 L to achieve a CO reduction from 4 to 1 percent (Colsman). The LTS in Georgetown University's 100 kW PAFC system reduces CO from 10 percent to 0.5 percent with less than 70 L of catalyst material and has a projected 25,000 hours life.

3.4 GAS CLEANUP SYSTEMS

Depending on the type of fuel cell, the reformer effluent may require additional CO removal and clean up of trace contaminants. PEMFCs are sensitive to both CO and higher hydrocarbon contaminants while PAFCs can operate directly on reformer product gas. For PEMFCs, CO levels must be below 100 ppm and ideally below the 20 ppm.

CO removal options include chemical and physical processes. In addition to the water gas shift reaction, chemical removal of CO can be accomplished through methanation or selective oxidation. Physical processes include adsorption and membrane separation.

Sulfur compounds poison catalysts and would inhibit the performance of nickel based shift catalysts and the catalyst on the PEMFCs. Sulfur compounds can be tolerated in the iron-based HTS but must be removed prior to the nickel-based LTS. Sulfur reacts with iron in the HTS and HTS catalyst performance deteriorates over time depending upon catalyst size. The following sections describe approaches for final gas clean up.

3.5 CO REMOVAL

3.5.1 Trace CO Removal

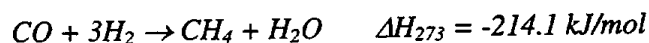
The CO content after the LTS ranges from 0.5 to 1 percent. This level is still too high for use in PEMFCs; however, it is sufficiently pure for other fuel cells. Both chemical and physical processes can separate hydrogen from reformer streams. Chemical processes include catalytic reaction of CO.

Not all of them are suited for the use in vehicles, due to costs, energy complexity or inability to reduce CO concentration. For the industrial process, pressure swing absorption (PSA) is the most common method to purify hydrogen. PSA is a single step process in which all impurities are simultaneously removed as the LTS effluent moves through the adsorbent bed. With a naphtha feed, hydrogen from PSA has a purity greater than 99.999 mole percent. The adsorbent bed has regularly be regenerated by depressurization followed by a purge of hydrogen. The size of a PSA system combined with the requirement for regeneration makes it unsuitable for use on vehicles.

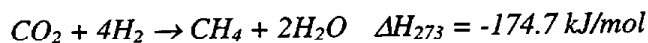
Other researchers expect that fuel cells will be more CO tolerant. Designs by ADL include PROX reactors to reduce CO, while HBT is investigating a humidified LTS to avoid further CO-cleanup (HyWeb).

3.5.2 CO Methanation

One side reaction, methanation (essentially the reverse of reforming), can take place with the hydrogen and CO present in the reformer product. Selective methanation was investigated by Colsman. The reaction proceeds according to the following highly exothermic reaction:



A parallel reaction converts CO₂ to methane. This exothermic reaction consumes hydrogen and generates heat without removing CO.



The theoretical equilibrium of the methanation reaction is below 10 ppm. Several researchers describe the methanation of CO with ruthenium catalysts (Kawatsu, Randhava). Experimental data with a rhodium/ruthenium catalyst on an alumina substrate achieve CO levels of 130 ppm (Baker). These results were achieved with 0.3 percent CO feed in the presence of high steam levels (20 percent) which favor CO production through the reverse water gas shift reaction. Space velocities ranged from 500 to 3000 h⁻¹ and temperatures ranging from 120 to 220°C. Kawatsu showed low CO levels as the catalyst temperature was lowered to 120°C (Figure 3-24). The heat of reaction poses a difficulty with all CO removal reactions. Lower temperatures favor lower CO levels; however, the reaction of CO raises the temperature of the gas stream.

Therefore, thermal management and minimizing initial CO levels will be an important part of CO removal processes.

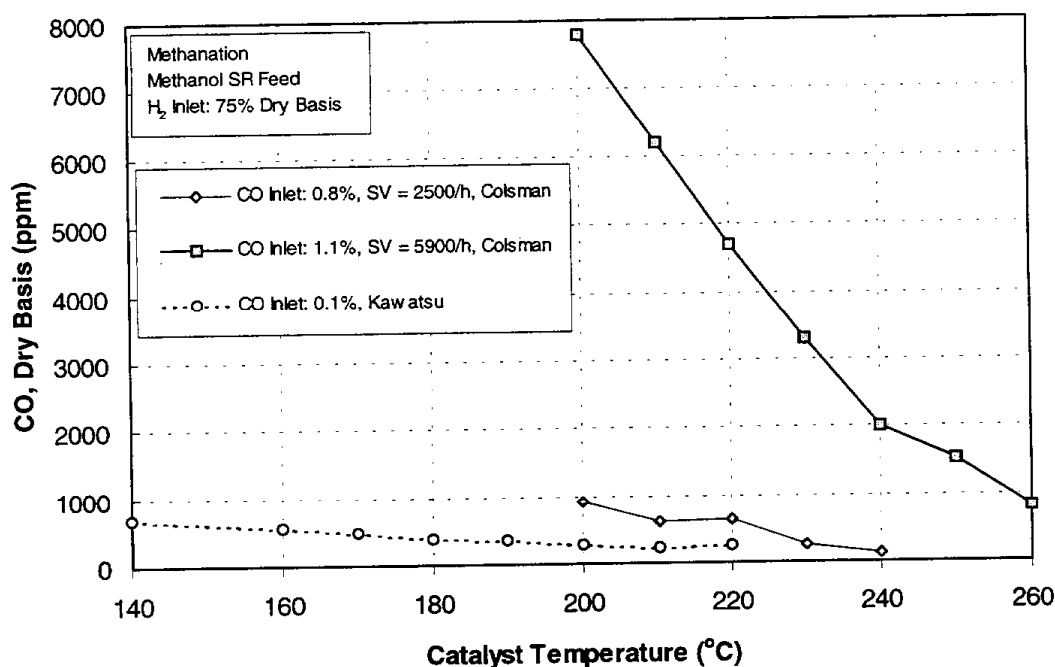
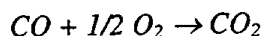


Figure 3-24. CO methanation data (Colsman, Kawatsu)

3.5.3 Selective CO Oxidation

Preferential oxidation (PROX) is a process where additional air is injected to oxidize CO to levels below 1 percent. A selective catalyst favors the reaction of CO with oxygen rather than the reaction with hydrogen. If 1 percent CO is converted to CO₂, 1 percent hydrogen will be converted to water vapor. The ratio of hydrogen consumption can be higher if temperature excursions occur in the PROX.

Selective oxidation or preferential oxidation of CO into CO₂ results in the lowest CO concentrations through the following reaction:



To implement this approach, a small quantity of air is injected into the LTS product gas. The reaction must occur at a low temperature with a selective catalyst that primarily oxidizes CO and not hydrogen.

Toyota investigated a platinum and ruthenium catalysts for selective CO oxidation with simulated methanol steam reformer product gas (Kawatsu). Data for space velocities ranging from 10,000 to 15,000 h⁻¹ were reported. The ruthenium catalyst was more effective than the platinum catalyst and maintained CO levels below 5 ppm over a temperature range of 100 to 160°C.

Amphlett reviewed sizing and design consideration for PROX systems. The key considerations to maintaining effective CO removal and minimizing reactor size are the following:

- Reduce reaction temperature to minimize reverse shift reaction
- Minimize inlet CO concentration
- Maximize operating pressure
- Increase oxidation rate through more active catalysts or increasing reaction temperature

Including ruthenium in the electrocatalyst of the PEMFC is another alternative for CO oxidation. Similar to the PROX approach, a small amount of air must be added to the hydrogen stream. Data from Toyota showed almost identical performance with hydrogen and hydrogen with 100 ppm CO on PEMFCs with platinum/ruthenium electrocatalysts.

Oxidation of CO may lead to premature aging of the membrane and sintering of the catalyst (Amphlett).

3.5.4 Membrane Gas Clean Up

Membranes can be used to separate hydrogen from other gases in the reformer product gas. The gas passes over a membrane and hydrogen passes through the membrane. A membrane system generally produces a gas stream with high hydrogen purity with some of the hydrogen in the membrane effluent. Membranes require high pressure to drive the gas transfer. Figure 3-25 shows the fraction of hydrogen that is recovered from the product gas from a methanol steam reformer (Colsman). The reformer gas is maintained at 20 atm. Hydrogen passes through the membrane and is referred to as the permeate. The fraction of hydrogen that is recovered depends upon the permeate pressure. As the permeate pressure drops, the hydrogen yield increases; however, the pressure available to the fuel cell decreases.

Actual membrane performance is below that of theoretical predictions. Data from Colsman in Figure 3-26 show that the highest hydrogen yield with a membrane system were obtained at low gas flow rates and membrane temperatures of 300°C. Under optimal conditions, hydrogen recovery was within 90 percent of the theoretical value. However, at higher gas flow rates and lower temperatures, the hydrogen recovery dropped below 60 percent of the theoretically achievable value.

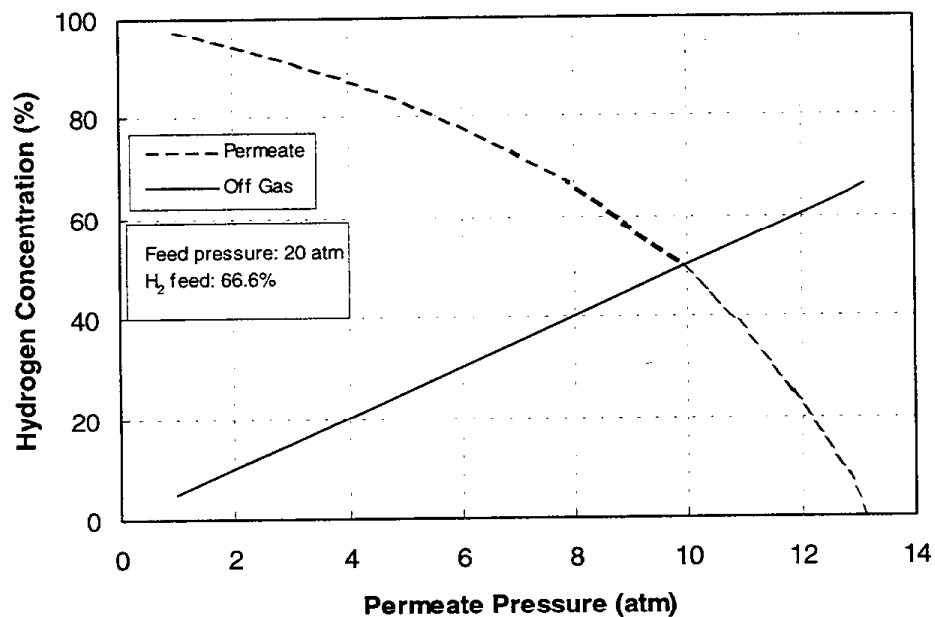


Figure 3-25. Predicted membrane performance with hydrogen/CO₂ feed

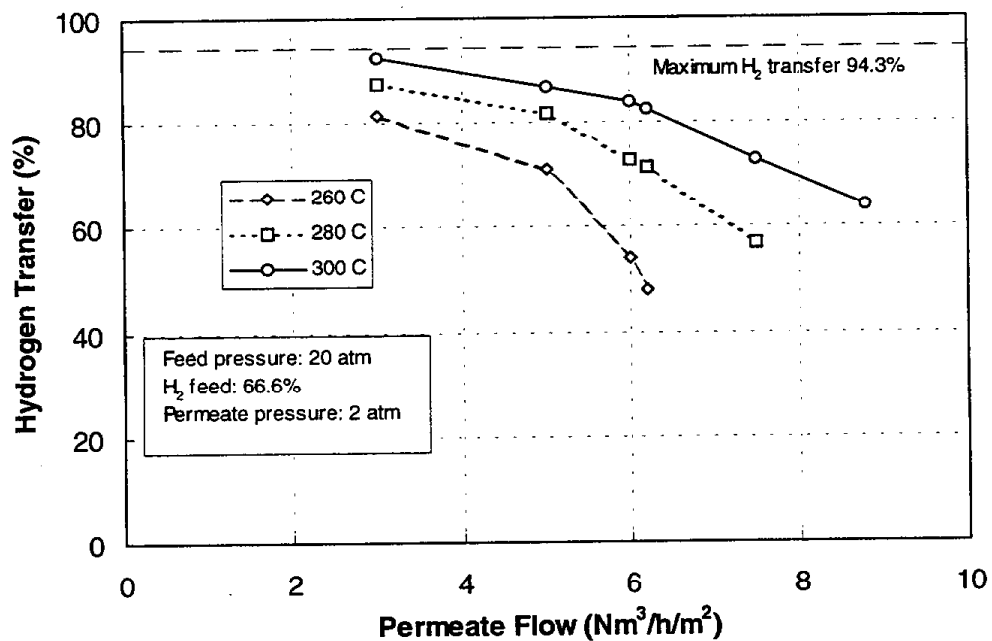


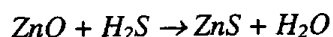
Figure 3-26. Membrane performance data (Colsman)

Membrane systems have the advantage of providing high purity hydrogen which improves fuel cell efficiency. The membrane requires very high upstream reformer gas pressures and a relatively high hydrogen concentration. Maintaining a high pressure is possible with a steam reformer system since both the methanol and feed water can be brought to a high operating pressure with liquid pumps without incurring significant energy penalties to generate the high pressure feed. The high pressure requirement does affect the design of the reformer, however, and will require thicker vessel walls and a heavier system. Using a membrane for a fuel cell system is still developmental.

3.5.5 Sulfur Removal

Sulfur compounds must be removed prior to the LTS to prevent poisoning of the catalyst. Experience with steam reformers indicates that sulfur levels below 0.5 ppm are desirable with levels below 0.1 ppm leading to improved catalyst life (Twigg). These low levels are necessary for commercial chemical processing plants that require operating runs on the order of 10,000 hours while vehicle lifetimes are closer to 2000 hours. Zinc Oxide (ZnO) absorbents in modern chemical plants will reduce sulfur levels in natural gas to 0.02 ppm.

ZnO reacts with hydrogen sulfide to produce zinc sulfide.



The reaction produces zinc sulfide and water vapor. Special absorbent material structures are required to accommodate the diffusion of water vapor away from the reaction and the morphological change of the zinc molecule. The spent zinc sulfide sorbent must be removed and used to remove sulfur compounds from the gas stream. For low sulfur streams (50 ppm in gasoline) the zinc oxide bed can be designed to last several years. The sulfur content in California on-road diesel fuel, is about ten times as high as that of gasoline. Consequently, the ZnO bed would need to be changed on a monthly basis. Zinc Oxide beds are effective over a temperature range from 200 to 500°C. Typical operating temperatures are around 400°C. The presence of steam suppresses the reaction to ZnS with the equilibrium H₂S concentration being proportional to the concentration of steam in the feed gas. At 400°C, equilibrium H₂S is 0.15 ppm with a feed gas composition containing 10 percent steam.

3.6 OTHER REFORMING TECHNIQUES

3.6.1 Catalytic Autothermal Reforming (ATR)

In addition to non catalytic POX, partial fuel oxidation can also be performed in the presence of a catalyst, which is known as autothermal reforming (ATR). The mixture of feed gases is set up to maintain the proper steam ratio for complete reforming and proper stoichiometry to maintain reaction temperature. This approach combines the catalytic aspect of the steam reforming technology with the in-situ oxidation of a POX. The operating temperature of an ATR is lower than that of a POX but higher than that of a SR. Two different types of catalyst are employed in autothermal reactors: the first is usually a platinum based combustion catalyst which facilitates rich combustion. The second is a conventional nickel based steam reforming catalyst. These

catalysts need protection from sulfur poisoning, thus requiring either a sulfur clean-up before the fuel enters the combustion chamber or sulfur free fuels. Furthermore, the control of oxygen is critical to prevent catalyst sintering due to temperature excursions (Cataquiz).

For autothermal reformers (ATR), a higher steam feed (H_2O/C) is used in the reactor feed. Unreacted methane compositions are higher initially and methane is converted in a reforming catalyst. The advantage of the ATR approach is a higher possible reformer efficiency than the PO only approach. A lower reactor temperature also eliminates the requirement for exotic materials. The ATR is prone to soot formation if the operating temperatures become too low in the reactor. Soot formation would be less likely with oxygenated fuels such as ethanol and methanol.

Arthur D. Little (ADL) (Cambridge, MA) has been working on POX and ATR systems for PEMFC vehicle applications. Reformer development activities have been "spun off" to Epyx Corporation, a wholly-owned subsidiary of ADL. Most of the ADL/Epyx work has involved ATR systems operating on gasoline and ethanol. Epyx has performed extensive evaluations of their ATR system (shown in Figure 3-27) including over 300 hours of operation on gasoline. The advantage of an ATR is that higher efficiencies are possible than with a POX unit; however, under adverse operating temperatures, high levels of methane can be produced (1 percent). When the operating temperatures and catalyst space velocity are carefully managed, low methane levels are achievable (Mitchell). Epyx has achieved a steady-state hydrogen production efficiency of 78 percent when operating on gasoline and 84 percent when operating on ethanol. Start-up times are currently reported as 10 minutes with developments underway to improve start-up, transient operation, packaging, and system size. Epyx packaged their fuel processor with a Los Alamos National Laboratory PROX and a Plug Power PEMFC to demonstrate an integrated PEMFC system that produced 10 kW_e of power.

Johnson Matthey is developing a catalytic partial oxidation reactor know as the Hot Spot™. This integrated reformer consists of small modules with passages for reactant inlet and hydrogen/product gas outlet. The system, shown in Figure 3-28, allows for rapid light off and modular operation. Several Hot Spot™ reactors would be packaged in a vehicle system. The number of units that operate could be varied to control load. The Hot Spot™ approach combines features of both partial oxidation and steam reforming. The reactor can be started quickly by operating in a partial oxidation mode. Once the reactor is at operating temperature, steam is added and the heat from partial oxidation provides the exothermic energy for steam reforming. This autothermal reforming approach demonstrated with the Hot Spot™ reactor is particularly suitable for methanol fuel. The methanol reforming reaction occurs at relatively low temperatures (260°C) and methanol does not readily form soot when it is combusted even under substoichiometric conditions. The autothermal reformer relies on internal heat transfer between the partial oxidation reactants and the feed steam to provide the heat for steam reforming. This approach makes an autothermal reformer more compact than a steam reformer.

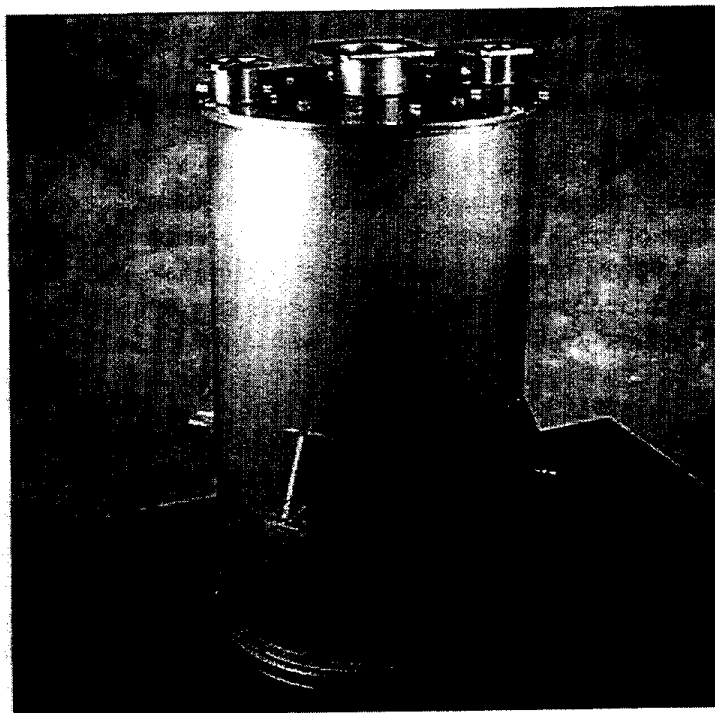


Figure 3-27. Epyx ATR 50 kW fuel processor

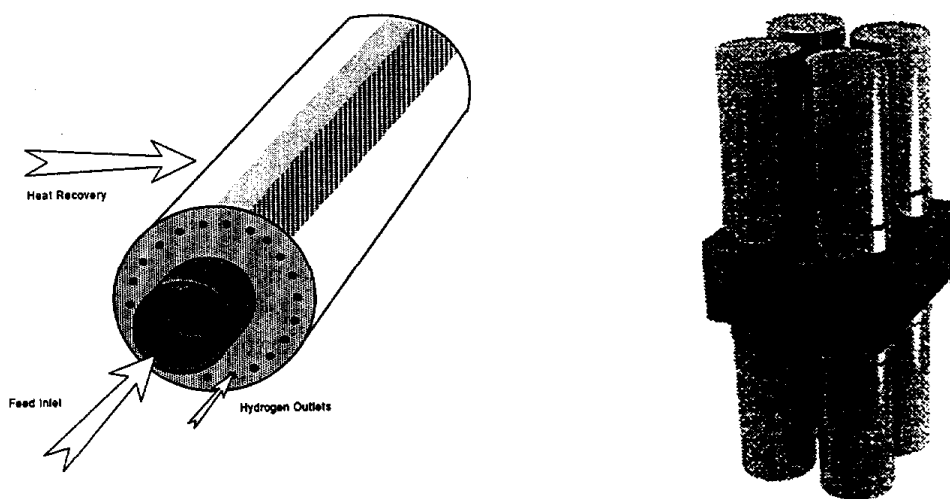


Figure 3-28. Johnson Matthey Hot Spot™ reactor

3.6.2 Internal Reforming Fuel Cells

Several fuel cells operate under conditions that convert the anode feed into reactants that are suitable for the fuel cell reaction. The DMFC dissociates methanol on the anode catalyst and therefore does not require a fuel processing system. Solid oxide fuel cells operate at temperatures which are high enough to reform fuels in the presence of steam, oxygen, and the fuel cell surface. However, combined reforming and fuel cell reaction may lead to thermal stresses on the ceramic materials. Therefore, SOFCs with an upstream reformer may be practical.

3.7 OTHER COMPONENTS AND PERFORMANCE PARAMETERS

3.7.1 Energy Storage

Fuel cell vehicles require storage capacity for the primary vehicle fuel as well as intermediate energy storage for hybrid systems. The energy density and the corresponding increases in vehicle weight affect the fuel consumption of vehicles and ultimately their emissions. Setting aside the weight and space limitations of hydrogen storage, the lack of infrastructure prevents pure hydrogen vehicles from achieving a large market share in the near term. Table 3-6 shows the weight and fuel storage capacity for various fuel storage options with the same energy content as 50 L of gasoline. The total weight of the fuel and fuel tank are calculated as the fuel tank weight is very significant for some storage options. The total fuel tank volume is shown since this value is used to determine fuel tank weight. The comparison of fuel storage options illustrates the volume and weight constraints for gaseous fuels. Fuel cells are more efficient than gasoline IC engines. Consequently, less fuel than the 50 L equivalent shown in Table 3-6 would be required to achieve the same range for fuel cell powered vehicles. The storage volumes could be reduced by a factor of over 2 for dedicated hydrogen fuel cell vehicles which are not analyzed further in this study. Fuel tank sizes were reassessed for the fuel cell vehicles considered in this study.

Table 3-6. Fuel storage performance parameters for 50-L gasoline equivalent (Deluchi, Colsman)

Fuel	Temperature (K)	Pressure (atm)	Total Weight* (kg)	Total Volume* (L)
Compressed H ₂	298	200	148	920
Compressed H ₂	298	670	190	510
H ₂ - Fe Ti Hydride	310 to 535	34	863	23.5
Liquid H ₂	25	5	75	312
Gasoline	298	1	42	61
Diesel	298	1	42	54
LPG	298	15	110	110
Methanol	298	1	95	95
Ethanol	298	1	71	71
CNG	298	200	160	260
LNG	130	5	120	130

*Includes fuel and tank.

Table 3-7 shows the estimated fuel tank capacity required for IC engine powered gasoline vehicles and fuel cell powered vehicles. In general, the fuel tank capacity is intended to provide the same range as that of a gasoline vehicle. The fuel cell powered vehicles are more efficient so the amount of fuel can be reduced as shown in Table 3-7. The fuel volume for the gasoline and diesel fuel cell vehicles was reduced to 40 L. This fuel volume provides a slightly higher range than that of the conventional gasoline vehicle. Fuel tank size is important since it not only affects vehicle range but also affects fuel spillage assumptions discussed in Section 6.2. The fuel tank volume represents a compromise between reducing vehicle weight and providing additional range. It was estimated that the benefits of achieving additional range outweighed the benefits of further reductions in fuel tank size. Commercial passenger cars with diesel IC engines tend to achieve a greater range than gasoline vehicles. This trend indicates that manufacturers do not choose to reduce fuel tank size if storage size is not an issue. Similarly, in this study, the size of the diesel tank is held the same as that of the gasoline fuel cell vehicle. LPG, methanol, ethanol, and CNG have a lower energy density than gasoline. Fuel tank volumes were calculated to achieve the same range as the gasoline fuel cell vehicle. The result is fuel tank storage volumes ranging from 55 to 80 L for the liquid fuels and 190 L for CNG. The fuel volumes correspond to the fuel energy shown in Table 3-7. As discussed in Section 4, methanol steam reformer vehicles are more efficient than POX fuel cell systems. Consequently the fuel tank size for this type of vehicle does not need to be as large as that for a methanol POX system. The tank size was also calculated for a CNG vehicle with reduced range.

Table 3-7. Estimated fuel tank capacities

Fuel	Fuel ^a Volume (L)	Density (g/mL)	Fuel Weight (kg)	Fuel Energy (MJ)	Fuel Tank (kg)	Total Weight (kg)
Gasoline ICE	50	0.72	36	1573	4.0	40
Gasoline POX PEMFC	40	0.72	28.8	1259	3.2	32.0
Diesel POX PEMFC	40	0.86	34.4	1500	3.2	37.6
LPG POX PEMFC	55	0.50	27.5	1265	4.4	31.9
Methanol POX PEMFC	80	0.79	63.2	1264	6.4	69.6
Methanol SR PEMFC	55	0.79	43.5	869	4.4	47.9
Ethanol POX PEMFC	59	0.785	46.3	1251	4.7	51.0
CNG POX PEMFC, @ 200 bar	190	0.142	27.0	1273	70	97.0
CNG POX PEMFC @ 200 bar	120	0.142	17.0	804	50.0	67.0

^aThe fuel tank size assumptions result in a 15 percent increase in range for gasoline, LPG, ethanol, methanol, and CNG POX PEMFC vehicles over a conventional gasoline vehicle on the city driving cycle. For diesel POX PEMFC and methanol SR PEMFC vehicles the increase in range is 30 and 15 percent, respectively.

^bTank size for a CNG vehicle with reduced range but less weight gain from fuel storage.

Hybrid vehicle configurations require intermediate energy storage to provide power for peak acceleration and accumulate energy during low power operation. The requirements for battery performance with hybrid vehicles are different than those of battery powered electric vehicles. The battery must meet requirements for energy storage as well as peak power for acceleration and hill climbing. With a smaller battery on hybrid vehicles, specific power will be an important consideration. The specific power for ultra capacitors is particularly high. Advanced batteries are under development for commercial production for battery powered electric vehicles and would also be available for hybrid vehicle. These parameters are compared in Table 3-8. Ultra capacitors still under development have longer term commercial prospects.

Table 3-8. Energy storage system performance parameters (Unnasch 1995, Kalhammer 1995, Murphy 1996)

Storage Device	Specific Energy (Wh/kg)	Energy Density (Wh/L)	Specific Power (W/kg)
<u>Batteries:</u>			
USABC mid-term goal	80 to 100	135	150 to 200
USABC long-term goal	200	300	400
Advanced lead acid	50	120	300 to 400
Nickel-metal hydride, 2004	80 to 120	150 to 275	180 to 250
Nickel-cadmium	50 to 60	110	150 to 180
Lithium-ion	120 to 140	250	200 to 300
<u>Ultra-Capacitors:</u>			
DOE near-term goal	5	7	1500
DOE advanced goal	15	20	1600
Maxwell Lab Carbon/ organic packaged	4.5	6	1000
LLNL Aerogel carbon/aqueous packaged	<2	1.5	2000

3.7.2 Gas Compression and Pumping

Fuel cell systems require pressurized air, water, and fuel for the feed into the fuel processor. The efficiency of pumps and compressors that perform these functions affects the efficiency of the overall fuel cell system.

Gas compression for fuel cell systems represent a significant portion of the parasitic power demand. Fuel cell operating pressures for vehicles will range from 1 to 4 atm. Operating at elevated pressures improves fuel cell efficiency as well as specific power. Steam reformer systems require compressed air for the cathode feed and POX systems require compressed air for the POX feed and cathode feed. The required air pressure is 3 to 5 atm. Both positive

displacement and aerodynamic compressors can provide the pressure needed for air flow. Examples of positive displacement designs are roots blowers, Volkswagen's G-Lader, and scroll compressors. These types of devices have been used as superchargers for automotive engines. Aerodynamic designs include axial flow compressors such as those used in aircraft turbines and centrifugal compressors such as automotive type turbochargers. Centrifugal compressors are compact in design but their efficiency falls off as the flow and pressure deviate from the design point. Table 3-9 lists a air compressors that are being developed for fuel cell systems.

Table 3-9. Air compressors under development for fuel cell applications (HyWeb)

Organization	Technology	Activity
Allied Signal	Turbo compressor	Develop compact light weight air compressor with improved low flow performance
A. D. Little	Scroll compressor expander	2 nd Generation compressor expander for PEMFC systems
CORAC	Turbo compressor	Motor driven turbo compressors for industrial applications.
Vairex	Variable displacement compressor	Compressor with constant pressure ratio of 3.2 over a turn down ratio of 10:1.

The projected performance of a turbo-compressor and expander turbine is shown in Figure 3-29. Efficiency represents the ratio of theoretical power required to actual power required. The net power requirements are calculated from the mass flow through the unit and pressure ratio. Turbo-expander systems are ideally designed if the power output from the expander exceeds the power demand from the compressor. The power demand from the expander can be met with supplemental fuel if required.

Parasitic electrical loads affect fuel cell power demand. The performance curve for a typical liquid pump is shown in Figure 3-30. This load dependence is incorporated into the vehicle performance model.

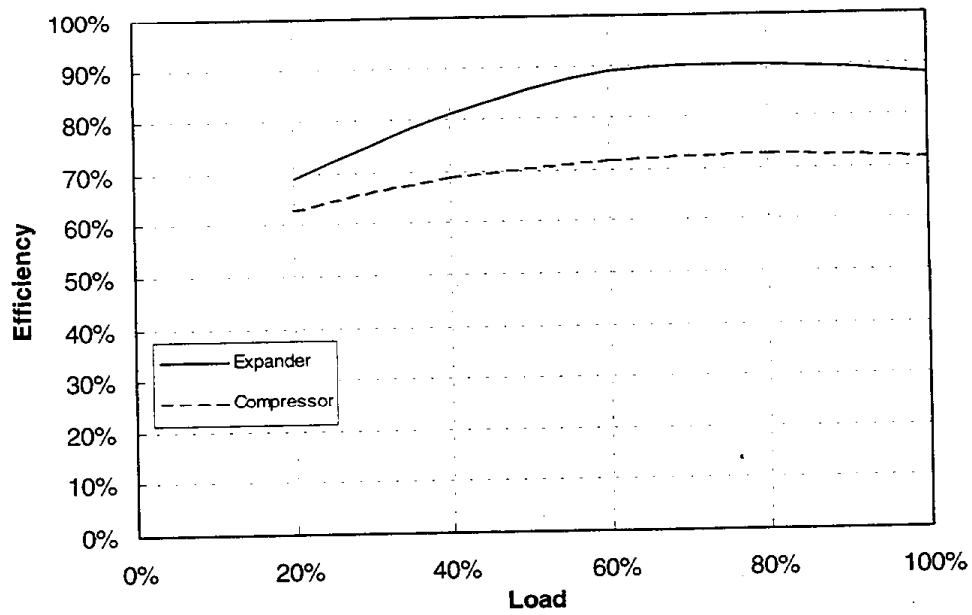


Figure 3-29. Projected compressor and expander performance curves

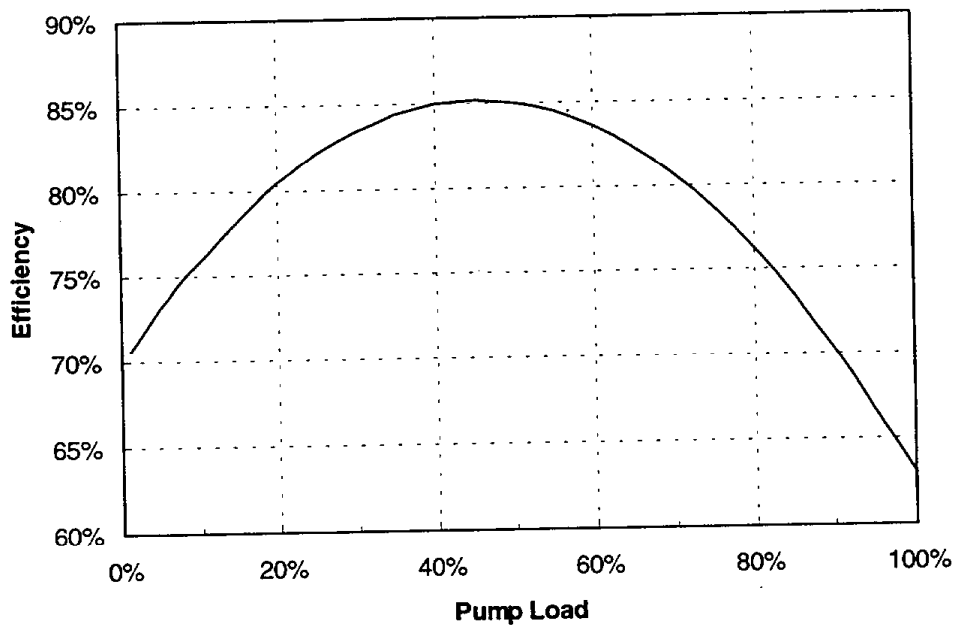


Figure 3-30. Performance of a typical pump

